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[Contribution from the Chemical Laboratory of the University of Wyoming.]

THE REPLACEMENT OF HALOGEN BY THE NITRO GROUP.

[FIRST PAPER.]

BY L. CHAS. RAIFORD AND FRED. W. HEYL.

It has long been known[1] that 2,4,6-tribromphenol can be made to interact with nitric acid in such a way that the halogen atom para to the hydroxyl group is replaced by a nitro group. Later it was found by Claus and Hirsch[2] that 2,4,6-tribrom-*m*-cresol gives similar results, and they reported the isolation of the para compound, 2,6-dibrom-4-nitro-*m*-cresol, as the product. But in no case, so far as we are aware, has more than one nitro compound been obtained at once as the result of the action specified.

In 1900 Zincke[3] undertook the nitration of 2,4,6-tribrom-*m*-cresol by treatment of a glacial acetic acid solution of the substance with solid sodium nitrite. From the reaction mixture thus obtained he reported the isolation of but a single substance, a mononitrodibrom-*m*-cresol in which the halogen

[1] Armstrong and Harrow: Jahres. d. Chem., **1876**, 448.
[2] J. prakt. Chem., [2] **39**, 61 (1889).
[3] *Ibid.*, [2] **61**, 564 (1900).

atom para to the hydroxyl group had been replaced by the nitro group. In an attempt to prepare stereoisomeric chlorimidoquinones, one[1] of us, working with Stieglitz, had occasion to repeat Zincke's work with tribrom-*m*-cresol, and found that when the reaction is allowed to proceed at a temperature of 12°–15° (Zincke gave no statement relative to the temperature at which he carried on his experiments) it gives a mixture of two isomeric mononitrodibrom-*m*-cresols, in which the nitro groups introduced are ortho and para, respectively, to the hydroxyl group. The ease with which this reaction took place, and the excellent yields of the isomers obtained, suggested the possibility of replacing halogen by the nitro group under similar conditions in other compounds. It was therefore decided to study the reaction more carefully, first with a well-known bromine derivative. Accordingly, 2,4,6-tribromphenol was selected for the starting material.

EXPERIMENTAL PART.

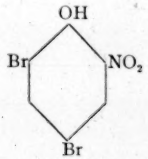
Nitration of Tribromphenol.—2,4,6-Tribromphenol,[2] prepared in the usual manner, carefully freed from tribromphenolbrom, and repeatedly crystallized from dilute alcohol until it melted constantly at 93° (uncorrected), was dissolved in about twelve times its weight of glacial acetic acid, and the resulting solution cooled to 12°–15°. To this was gradually added ten per cent. more than the calculated amount of solid sodium nitrite, during which time the flask was continually shaken and the temperature kept down to that specified above. When all the nitrite had dissolved the dark-colored liquid was poured, with stirring, into five volumes of cold water, and the mixture allowed to stand for some hours. At the end of this time the yellow solid was collected on a filter, washed with water, and dried on a porous plate. The weight of the mass at this point represented 97 per cent. of the theoretical yield, calculated on the basis of the formation of mononitro compounds alone.[3] The crude product began to

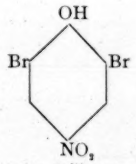
[1] Results soon to be published from the Kent Chemical Laboratory of the University of Chicago.

[2] Laurent: Ann. Chem. (Liebig), **43**, 212.

[3] As will be shown later, a portion of this was unchanged tribromphenol.

melt at 74° and was completely liquid at 94°—behavior that indicated the possible presence of more than one compound. It may be stated at once that two isomeric mononitrodibromphenols were isolated from the mixture,





4,6-dibrom-2-nitrophenol, melting at 117°, and 2,6-dibrom-4-nitrophenol, melting at 141°.

Separation of the Isomers.

The Para Compound.—Consideration of the properties of the two dibromnitrophenols recorded by Beilstein led, at first, to the attempt to separate them by distillation with steam, but this was found to be unsatisfactory. Separation by fractional crystallization of their potassium salts was found to be possible, though it involved much time. The best method of separation depends on the difference in solubility of the isomers in a mixture of chloroform and ligroin. A portion of the dried crude product, secured as indicated above, was dissolved in warm chloroform (1 gram to 0.75 cc.) and to the clear solution was added two volumes of ligroin, boiling at 40°–60°. Precipitation of nearly all the high-melting isomer (para compound) took place at once. After standing half an hour the solid was removed by filtration and crystallized twice from benzene, when nearly colorless crystals, melting at 141° and decomposing when heated above this point, were secured. In order to show that the compound here isolated is identical with 2,6-dibrom-4-nitrophenol, a small quantity of the latter was prepared by brominating 4-nitrophenol.[1] A mixture of the two products melts at the same temperature as either of them separately. The product ob-

[1] Brunck: Z. Chem., **1867**, 204.

tained by nitrating tribromphenol was analyzed for bromine.

0.1563 gram substance gave 0.1976 gram AgBr.

	Calculated for $C_6H_3O_3NBr_2$.	Found.
Br	53.87	53.82

The Ortho Compound.—When the filtrate obtained by removal of the para compound was allowed to evaporate to dryness it left a yellow solid melting at 80°–90°. This was crystallized several times from 95 per cent. alcohol until crystals melting constantly at 117° were secured. Some of this product was mixed with 4,6-dibrom-2-nitrophenol prepared according to Goldstein's[1] directions, and the mixture melted at 117°, showing the products to be identical. Analysis of the product obtained from tribromphenol gave the following result:

0.1329 gram substance gave 0.1689 gram AgBr.

	Calculated for $C_6H_3O_3NBr_2$.	Found.
Br	53.87	54.08

The mother liquor left after removal of the ortho compound was evaporated to dryness and gave a yellow solid that melted at 70°–77°, and which was thought, at first, to consist of traces of the ortho body, with possibly a third nitro compound. The material was purified by conversion into the barium salt in the usual way, and the latter was obtained in the form of yellow needles arranged in fan-shaped clusters, containing one molecule of water of hydration. A portion of this salt was dissolved in water and decomposed by dilute hydrochloric acid, when a colorless substance was secured. This was crystallized from dilute alcohol, out of which it separated in the form of long silky needles melting at 93°. A mixture of this substance with the tribromphenol used as starting compound still melted at 93°. Analysis of the recovered material for bromine resulted as follows:

[1] J. russ. chem. Ges., **10**, 354.

0.2028 gram substance gave 0.3446 gram AgBr.

	Calculated for $C_6H_2OBr_2$.	Found.
Br	72.50	72.37

A second portion of the barium salt mentioned above was heated to constant weight at 110°–115°, and the residue was then analyzed for barium:

0.1820 gram crystals lost, on drying, 0.0042 gram H_2O.

0.1820 gram crystals gave 0.0520 gram $BaSO_4$.

	Calculated for $(C_6H_2OBr_2)_2Ba.H_2O$.	Found.
H_2O	2.20	2.30
Ba	16.84	16.81

The Behavior of Trichlorphenol.—In an attempt to prepare the dihalogenated nitro-*m*-cresols, Raiford[1] found that while the dibromnitro-*m*-cresols could easily be obtained by treatment of 2,4,6-tribrom-*m*-cresol in glacial acetic acid solution with sodium nitrite, 2,4,6-trichlor-*m*-cresol could not be made to undergo the reaction. It became a matter of interest, therefore, in the present investigation, to examine 2,4,6-trichlorphenol in this direction. A portion of the compound was prepared by a modification of Chandelon's[2] method, which involved a much simpler, cleaner and more rapid method of securing the necessary hypochlorite solution. The latter was obtained according to Graebe's[3] method, and was then used as specified by Chandelon. The trichlorphenol obtained was carefully purified by dissolving it in a solution of sodium hydroxide, and treating this solution with carbon dioxide, which precipitated pure trichlorphenol, melting at 68°. When this was dissolved in glacial acetic acid, and sodium nitrite was mixed with the solution, as detailed above, the solid that separated when this solution was poured into water melted at 68°, and was, in fact, unchanged 2,4,6-trichlorphenol, which shows that the chlor compound is far less re-

[1] Unpublished reports.

[2] Bull. Soc. Chim., **38**, 116 (1882).

[3] Ber. d. chem. Ges., **35**, 43 and 2753 (1902).

active, under the conditions of this experiment, than the corresponding brom compound. Analysis of the recovered material for halogen gave the following result:

0.1040 gram substance gave 0.2254 gram AgCl.

	Calculated for $C_4H_2OCl_2$.	Found.
Cl	53.89	53.61

The work will be continued in this laboratory.

LARAMIE, WYOMING,
January, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXX.—ON ALKYLATION OF AROMATIC AMINO ACIDS: 5-IOD-2-AMINOBENZOIC ACID AND 3,5-DIIOD-2-AMINOBENZOIC ACID.

[SECOND PAPER.]

BY HENRY L. WHEELER AND CARL O. JOHNS.

When the salts of *o*-, *m*- and *p*-aminobenzoic acids are treated with alkyl halides, nitrogen alkyl derivatives result. From the work which has been published on this subject it appears that the action first takes place by addition, and then substitution, in the amino group, and no direct replacement of the metal by the alkyl group occurs. After substitution of hydrogen in the amino group, the alkyl group may then attach itself to oxygen and form an ester, either by directly replacing the metal of the carboxyl or by a rearrangement of a betaine.

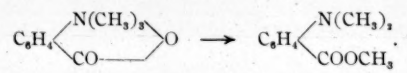
Griess[1] found that the potassium salt of *m*-aminobenzoic acid and ethyl iodide, in whatever proportion they were mixed, gave a mixture of mono- and diethylaminobenzoic acids.

The above potassium salt and allyl iodide invariably gave only a diallylaminobenzoic acid and no trace of a mono derivative. On the other hand, the potassium salt of aminoanisic

[1] Ber. d. chem. Ges., **5**, 1038 (1872).

acid and methyl iodide gave a monomethylaminoanisic acid.

In his next article Griess[1] showed that *m*-aminobenzoic acid gives, with three molecular proportions of potassium hydroxide and three of methyl iodide, the hydriodide of the deliquescent benzbetaine, trimethylaminobenzoic acid, when the residue, after evaporation, is treated with hydriodic acid. The betaine is a crystalline solid which loses one molecule of water at 105° and which, on heating, rearranges into methyldimethylaminobenzoate (oil):



Trimethylanisbetaine was prepared and found to behave in a similar manner.

Michler[2] heated *p*-aminobenzoic acid with three molecular proportions of potassium hydroxide and two of methyl iodide and obtained *p*-dimethylaminobenzoic acid. The diethylamino acid was then prepared in a similar manner.[3]

Michael and Wing, in a paper on the action of alkyl iodides on amino acids, state that in the case of *p*-aminobenzoic acid three molecular proportions of methyl iodide and an excess of potassium hydroxide give the mono- and dimethylamino acids and also the betaine. With ethyl iodide no betaine was obtained, the product being the ethyl ester of the diethylamino acid, $(C_2H_5)_2NC_6H_4COOC_2H_5$, and with three proportions of allyl iodide and an excess of alkali the sole product was diallylaminobenzoic acid. They state that they were unable to find that either the betaine or the allyl ester of the acid were ormed.

In 1893 Lauth[4] examined the behavior of *o*-aminobenzoic acid, neutralized with sodium hydroxide, towards two molecular proportions of methyl iodide in alcoholic solution, and obtained the dimethylaminobenzoic acid. The dimethyl-

[1] Ber. d. chem. Ges., **6**, 586 (1873).
[2] *Ibid.*, **9**, 401 (1876).
[3] *Ibid.*, **9**, 1912 (1876).
[4] Bull. Soc. Chim., [3] **9**, 970 (1893).

amino derivatives of the *meta* and *para* acid were likewise prepared. From the *ortho* acid he also obtained the quaternary derivatives, $NaO.COC_6H_4N(CH_3)_3I$, $HOCOC_6H_4N(CH_3)_3I$, and $HOCOC_6H_4(CH_3)_3OH$. The first of these quaternary derivatives was best obtained by allowing three molecular proportions of methyl iodide to act on the sodium salt of anthranilic acid. The formation of this compound goes to show that the first product of the reaction is not an ester. The monomethylanthranilic acid was prepared in a similar manner by Fortmann.[1]

H. Meyer[2] found, in 1900, that by the action of alkyl iodides on the potassium salt of *o*-aminobenzoic acid dissolved in 10 parts of water an excellent yield of the monoalkylamino derivatives was obtained. He prepared in this manner monomethyl-, ethyl-, normal propyl-, isobutyl- and isoamylanthranilic acids. Chloracetic acid[3] and ethylene bromide[4] also give *N*-derivatives.

The point to be emphasized in the above researches is that no one has observed the formation of esters of the type

$$H_2NC_6H_4COOR$$

by the action of alkyl halides on the alkali salts of the simple aminobenzoic acids.

On the other hand, by the above method, certain substituted aminobenzoic acids give esters of this type in which the hydrogen of the amino group is not substituted and from which the unaltered acid can be obtained by saponification.

The writers' attention was called to this fact when in a recent investigation it became desirable to characterize 3,5-diiod-4-aminobenzoic acid[5] by a derivative having a melting point. It was then found that the potassium salt of this acid and ethyl iodide gave an ester and not an alkylamino acid.

A search in the literature has revealed the fact that not only

[1] J. prakt. Chem., [2] **55**, 123 (1897).
[2] Monats. Chem., **21**, 932.
[3] Mauthner and Suida: Monats. Chem., **9**, 728 (1888); **11**, 380 (1890).
[4] Schiff and Parenti: Ann. Chem. (Liebig), **226**, 244 (1884).
[5] This Journal, **42**, 455 (1909).

the silver salt of 3,5-dinitro-4-aminobenzoic acid[1] but also 3-nitro-2-aminobenzoic acid, either in the form of the silver salt at 20°–100°[2] or the potassium salt at 130°–140°,[3] gave an ester.

The result in the case of the mononitroamino acid is noteworthy since two other isomeric mononitroamino acids have been examined and have been found to alkylate on the amino group.

Rollwage[4] states that 3-nitro-5-aminobenzoic acid gives a *N*-ethyl acid, while Wheeler and Barnes[5] obtained from the silver salt of 4-nitro-2-aminobenzoic acid the *N*-compounds

$$C_2H_5NHC_6H_3.NO_2COOH$$

and, in smaller amount,

$$C_2H_5NHC_6H_3NO_2COOC_2H_5.$$

It will be noticed in all the above cases that when the amino group is surrounded by two substituents or radicals, I and I, COOH and NO_2, or NO_2 and NO_2, alkylation takes place on the oxygen and not on the nitrogen.

In accordance with this, we now show that 5-iod-2-aminobenzoic acid gives a *N*-alkyl derivative, while 3,5-diiod-2-aminobenzoic acid gives an ester. In the latter case the adjacent groups are COOH and I.

Whether this difference in behavior is due to stereochemical interference or to both this influence and that of negative groups—the above substituents have a negative character—must be left to be investigated, and we wish to reserve the work for this laboratory.

It would be expected that substituted aromatic amino acids would share, at least to some extent, the properties of the corresponding substituted aromatic amines. Stereochemical interference or retardation (*sterische Verlangsamung*[6])

[1] Salkowski: Ann. Chem. (Liebig), **163,** 11 (1872).
[2] Hübner: *Ibid.*, **195,** 40 (1879).
[3] Zacharias: J. prakt. Chem., **43,** 437 (1891).
[4] Ber. d. chem. Ges., **10,** 1704 (1877).
[5] This Journal, **20,** 217 (1898).
[6] Bischoff: Jahrbuch d. Chem., **1903,** 172

has frequently been noted in the various stages of alkylation in these cases. It has been observed among aromatic amines that groups in both of the *ortho* positions (alkyl, phenyl, bromine, nitro and acetamino) completely[1] prevent the formation of quaternary bases and that a single *ortho* substituent reduces the rate or tendency of the amine to alkylate;[2] while 1-methyl-2-amino-3-isobutylbenzene, at 150°, is attacked to only a slight extent[3] and diaminomesitylene is not altered at all by alkyl halides.[4] Methyl sulphate has been found to alkylate where alkyl halides fail.

On the other hand, groups in the *ortho* positions to the carboxyl fail to prevent the alkylation of this group by alkyl halides[5] and it also appears that groups situated in the same manner in reference to a hydroxyl do not protect this group from alkylation, as, for example, in 3,5-diiod-4-hydroxybenzoic acid[6] and 3,5-diiodtyrosine.[7]

The results obtained in the alkylation of substituted amino acids not only have theoretical significance but they also may prove to be of practical value in separating mixtures of acids and isolating the adjacent derivatives. Some of these acids, which are frequently formed among isomers in smallest amount, have been obtained from mixtures only by tedious crystallizations of their salts.

We have also found that 3,5-diiod-2-aminobenzoic acid gives an acid chloride when it is suspended in benzene and phosphorus pentachloride is added. The product with alcohol gives the same ester as is obtained by alkylating the potassium salt with ethyl iodide.

When the acid chloride is treated with potassium sulphydrate it yields the potassium salt of 3,5-diiod-2-aminothiolbenzoic

[1] Hofmann: Ber. d. chem. Ges., **5**, 718 (1872). Fischer and Windaus: *Ibid.*, **33**, 345, 1967 (1900). Pinnow: *Ibid.*, **32**, 1401 (1899); **34**, 1129 (1901).

[2] Fries: Ann. Chem. (Liebig), **346**, 190 (1906).

[3] Effront: Ber. d. chem. Ges., **17**, 2317 (1884).

[4] Morgan: P. Chem. Soc., **18**, 87 (1902). Schmidt: Ueber den Einfluss der Kernsubstitution auf die Reaktionsfähigkeit aromatischer Verbindungen; Chem. u. chem.-tech. Vorträge, **8**, 314 (1902).

[5] Sudborough: J. Chem. Soc., **67**, 587 (1895).

[6] This Journal, **42**, 460 (1909).

[7] *Ibid.*

acid, from which we have prepared and examined the thiol acid and its disulphide. This is probably the first representative of a thiol acid containing a free amino group.

EXPERIMENTAL PART.

2-Amino-5-iodbenzoic Acid, $C_6H_3\begin{cases}COOH\ (1)\\NH_2\ (2)\\I\ (5)\end{cases}$.—This acid was first obtained by Grothe.[1] Its structure was determined by Wheeler and Liddle[2] by oxidizing 1-methyl-2-acetylamino-5-iodbenzene with potassium permanganate. It is far more easily obtained by directly iodating anthranilic acid.

Five grams of anthranilic acid were dissolved in 50 cc. of water containing 2.1 grams of potassium hydroxide. Nine and two-tenths grams of powdered iodine were added in small portions and the mixture was frequently shaken. The iodine was rapidly absorbed, causing the formation of a brown precipitate. This crude product weighed 9.0 grams, or 93 per cent. of the calculated. When crystallized from alcohol it formed colorless prisms that decomposed at 210°. When mixed with a sample of 2-amino-5-iodbenzoic acid from our previous work, the mixture also melted at 210°.

	Calculated for $C_7H_6O_2NI$.	Found.
N	5.32	5.55

Action of Ethyl Iodide on the Potassium Salt.—One gram of potassium hydroxide was dissolved in 40 cc. of water and 4.7 grams of pulverized 2-amino-5-iodbenzoic acid were added to the solution. A slight trace of acid remained undissolved and was filtered off. The solution was mixed with 60 cc. of alcohol and 15 grams of ethyl iodide and this mixture was heated for 3 hours on a water bath. When the solution was evaporated to dryness it left a residue which dissolved completely in ammonia and was reprecipitated by acetic acid in small clusters of minute prisms. The yield was 71 per cent.

[1] J. prakt. Chem., [2] **18**, 326 (1878).
[2] This Journal, **42**, 499 (1909).

The product melted to a black oil with effervescence at 162° and the melting point was not raised by recrystallizing twice from alcohol. It is easily soluble in ether, hot benzene and alcohol, and insoluble in water. Its solubility in dilute ammonia and the following analysis showed that it was not an ester. The acid had therefore alkylated on the nitrogen, forming *2-ethylamino-5-iodbenzoic acid.*

0.1790 gram substance gave 0.1450 gram of AgI.

	Calculated for $C_9H_{10}O_2NI$.	Found.
I	43.64	43.77

2,5-Diiodbenzoic Acid.—Five grams of 2-amino-5-iodbenzoic acid were added to a mixture of 50 cc. of concentrated hydrochloric acid and 150 cc. of water. Some of the acid remained undissolved. The whole was cooled with ice and diazotized with 2 grams of sodium nitrite dissolved in a little water. A colorless solution was obtained and to this was added an aqueous solution of 13 grams of potassium iodide. A dark green precipitate was formed when the mixture stood in ice for one hour; it was gently heated and nitrogen was evolved. The excess of iodine was removed by the addition of sodium bisulphite. The red precipitate remaining after this treatment weighed 7.1 grams, which is the theoretical yield. The acid was purified by dissolving in dilute ammonia and reprecipitating with hydrochloric acid. The portion for analysis was further purified by crystallizing from dilute alcohol. It formed slender prisms that melted to an oil at 183°. It was very soluble in alcohol and ether and moderately soluble in boiling benzene, from which it crystallized in needles. It was insoluble in water.

0.1842 gram substance gave 0.2313 gram AgI.

	Calculated for $C_7H_4O_2I_2$.	Found.
I	67.92	67.85

The Sodium Salt.—2,5-Diiodbenzoic acid gave a sodium salt which was very soluble in water. It crystallized from concentrated solution when cooled with ice. A dilute aqueous

solution gave white precipitates with silver nitrate, lead acetate, and mercuric chloride. It gave a green precipitate with copper sulphate but did not give a precipitate with barium chloride. The precipitates were not changed in appearance by boiling in water.

Ethyl 2,5-Diiodbenzoate.—One gram of the acid was boiled for 6 hours in 40 cc. of alcohol containing 5 drops of sulphuric acid. The resulting solution was concentrated to a small volume and made neutral with ammonia and evaporated to dryness. The product was crystallized from alcohol. It formed colorless, silky needles, which melted at 65°. It was easily soluble in ether, benzene and hot alcohol.

0.2009 gram substance gave 0.2359 gram AgI.

	Calculated for $C_9H_8O_2I_2$.	Found.
I	63.18	63.51

2-Amino-3,5-diiodbenzoic Acid, $C_6H_2\begin{cases}\text{COOH} & (1)\\ \text{NH}_2 & (2)\\ \text{I} & (3)\\ \text{I} & (5)\end{cases}$.—At first an attempt was made to prepare a diiodamino acid from the potassium salt of the above 5-iod-2-aminobenzoic acid by the direct action of iodine, in aqueous solution. When the materials were mixed in molecular proportions the action took place on warming on the steam bath. The product, instead of being an acid, however, proved to be 2,4,6-triiodaniline.

The desired acid was then obtained by the use of iodine monochloride. Five grams of 2-amino-5-iodbenzoic acid were dissolved in 200 cc. of 5 per cent. hydrochloric acid by the aid of heat. Four grams of iodine monochloride were then added to this solution. An immediate precipitate resulted and this increased by heating the mixture on a steam bath. The yield was 6.5 grams, which is 90 per cent. of the calculated. The product contained a trace of triiodaniline, which was removed by dissolving the precipitate in dilute ammonia, filtering and precipitating the acid with acetic acid. It was then purified by crystallizing from alcohol, whereupon it formed radiating

clusters of slender prisms that melted to a black oil at 230°–232°. It was very soluble in ether, difficultly soluble in hot benzene, and insoluble in boiling water.

0.1869 gram substance gave 0.2262 gram AgI.

	Calculated for $C_7H_5O_2NI_2$.	Found.
I	65.23	65.40
N	3.60	3.54

It was found that 2-amino-3,5-diiodbenzoic acid could easily be prepared by the action of 2 molecular proportions of iodine monochloride on anthranilic acid. By this method the yields varied from 85 to 90 per cent. Five grams of anthranilic acid were dissolved in 100 cc. of 5 per cent. hydrochloric acid. Sixteen grams of iodine monochloride in 100 cc. of water were added and the mixture was heated on the steam bath for a few minutes. The precipitate weighed 12 grams and was found to be identical with the above diiodaminobenzoic acid.

Proof of Structure of the Diiodaminobenzoic Acid.—Five grams of the diiodaminobenzoic acid were dissolved in 15 cc. of concentrated sulphuric acid. The solution was cooled in a freezing mixture and 1.2 grams of powdered sodium nitrite were added. The mixture was poured on crushed ice and the resulting solution added gradually to 2 volumes of boiling alcohol by pouring through a condenser. The alcoholic solution was boiled for 15 minutes and poured into cold water when it gave a bulky white precipitate. This crystallized from alcohol in clusters and warts of fine prisms that melted at 235°. When mixed with a sample of *3,5-diiodbenzoic acid*,[1] prepared by Dr. Liddle, the melting point was not changed.

The Ammonium Salt of 2-Amino-3,5-diiodbenzoic Acid.—The crude, more or less colored, acid obtained by the action of iodine monochloride on anthranilic acid, was easily purified by means of the ammonium salt. When a solution of the acid in hot dilute ammonia was cooled, the ammonium salt

[1] This Journal, **42**, 505 (1909).

separated in long, slender crystals. These were easily soluble in warm water but difficultly in cold. When this salt is heated or dried over calcium chloride it dissociates and the product becomes insoluble in water. On acidifying the solution with acetic acid, 2-amino-3,5-diiodbenzoic acid was precipitated in a very pure state.

The *sodium salt* of 2-amino-3,5-diiodbenzoic acid was very soluble in hot water and moderately soluble in cold. It crystallized in slender prisms and a solution of this salt gave white precipitates with silver nitrate, mercuric chloride, lead acetate and barium chloride. A yellowish green precipitate was formed with copper sulphate. These precipitates were not changed when boiled with water.

2,3,5-Triiodbenzoic Acid.—Five grams of 2-amino-3,5-diiodbenzoic acid were dissolved in 15 cc. of concentrated sulphuric acid and 1.2 grams of powdered sodium nitrite were added in small portions. The mixture was kept cold with ice and after standing one hour was poured on crushed ice. The resulting solution was filtered to remove a small quantity of insoluble substance and the filtrate mixed with an aqueous solution of 5 grams of potassium iodide. The whole was then heated on the steam bath and the free iodine was removed by the addition of sodium hyposulphite. This treatment gave an orange-colored precipitate which weighed 5.7 grams, or 90 per cent. of the calculated. It was very soluble in hot alcohol and crystallized in radiating clusters of slender, colorless prisms that melted at 224°–226°. It was easily soluble in ether, difficultly soluble in boiling benzene and insoluble in hot water.

0.1489 gram substance gave 0.2105 gram AgI.

	Calculated for $C_7H_3O_2I_3$.	Found.
I	76.20	76.38

The *sodium salt* of 2,3,5-triiodbenzoic acid was easily soluble in hot and moderately soluble in cold water. It crystallized in clusters of slender prisms and its aqueous solution gave white precipitates with silver nitrate, barium chloride,

mercuric chloride, and lead acetate, and a green precipitate with copper sulphate.

2-Amino-3,5-diiodbenzoyl Chloride, $C_6H_2\begin{cases}COCl\ (1)\\NH_2\ (2)\\I\ (3)\\I\ (5)\end{cases}$. — Ten grams of powdered 2-amino-3,5-diiodbenzoic acid were suspended in 75 cc. of benzene, and 6 grams of phosphorus pentachloride added. The mixture was shaken from time to time until complete solution resulted. The reaction took place readily at the temperature of the room and was complete within an hour. The solution was filtered to remove a trace of suspended material and then used for the following experiments.

An attempt was made to obtain the chloride in a pure state by evaporating the benzene solution under diminished pressure at a temperature not exceeding 40°. This left a crust in the distilling bulb. Some dry ether was added and the evaporation repeated. The residue was very soluble in ether but in trying to crystallize it from ether and benzene it changed to a substance that did not dissolve in ether. As the crude chloride gave good results no further attempt was made to purify it.

2-Amino-3,5-diiodbenzamide.—A benzene solution of the chloride, made from 5 grams of the acid, was poured on 20 grams of powdered ammonium carbonate. The mixture was evaporated to dryness and the residue was washed with water. This treatment left 4.5 grams of gray crystalline material, which proved to be insoluble in dilute sodium hydroxide. It did not dissolve in water, chloroform o acetic acid. It was sparingly soluble in boiling alcohol and crystallized in long pointed needles. These began to decompose slowly at 230° and melted with decomposition at 238°–239°. They did not contain phosphorus.

	Calculated for $C_7H_6ON_2I_2$.	Found.
N	7.21	7.26

Ethyl 2-Amino-3,5-diiodbenzoate, $C_6H_2\begin{cases}COOC_2H_5 & (1)\\ NH_2 & (2)\\ I & (3)\\ I & (5)\end{cases}$. *From the Chloride and Alcohol.*—A solution of 2-amino-3,5-diiodbenzoyl chloride in benzene was mixed with ethyl alcohol and the mixture was evaporated to dryness. The residue was crystallized from alcohol and formed slender prisms that melted at 101°.

From the Potassium Salt and Ethyl Iodide.—Three grams of ethyl iodide were allowed to act on 3 grams of the potassium salt of 2-amino-3,5-diiodbenzoic acid dissolved in 60 cc. of ethyl alcohol. The mixture was heated for 2 hours, then the solution was evaporated and the residue treated with dilute ammonia. The ester which remained insoluble was crystallized from alcohol. It melted at 101° and was identical with the ester obtained from the acid chloride, a mixture of the substances obtained by the two methods melting at 101°. The yield of ester in this case was only about 32 per cent. On acidifying the ammonia solution used for separating unaltered acid from the ester a precipitate of the acid was obtained. The acid did not alkylate on the nitrogen.

0.2037 gram substance gave 0.2300 gram AgI.

	Calculated for $C_9H_9O_2NI_2$.	Found.
I	60.91	61.00
N	3.32	3.59

An attempt was made to alkylate 2-amino-3,5-diiodbenzoic acid on the nitrogen by using four molecular proportions of potassium hydroxide and eight of ethyl iodide to one of the acid, as follows: Five grams of 2-amino-3,5-diiodbenzoic acid were dissolved in 100 cc. of 95 per cent. alcohol containing 3 grams of potassium hydroxide. Sixteen grams of ethyl iodide were added and the mixture was heated until it ceased to give an alkaline reaction. This solution was evaporated and the dry residue treated with ammonia. The yield was 2 grams of ester melting at 101°, and 3 grams of unaltered acid

were recovered from the ammonia solution. There was no evidence of alkylation on the nitrogen.

In another experiment 2 grams of the ester were dissolved in 15 grams of ethyl iodide, no other solvent being used. The solution was allowed to stand for four days at ordinary temperature. At the end of this time nothing separated and there was no evidence of any reaction. The ethyl iodide was allowed to evaporate spontaneously and the residue, without purification, melted at 99°. On recrystallization from alcohol it melted at 101° and was found to be unaltered ester.

2-Amino-3,5-diiodthiolbenzoic Acid, $C_6H_2\begin{cases}COSH & (1)\\ NH_2 & (2)\\ I & (3)\\ I & (5)\end{cases}$.—A benzene solution of 2-amino-3,5-diiodbenzoyl chloride, made from 10 grams of 2-amino-3,5-diiodbenzoic acid, was slowly filtered into an alcoholic solution of potassium sulphydrate made by saturating a solution of 14 grams of potassium hydroxide in 100 cc. of 95 per cent. alcohol with hydrogen sulphide. The potassium sulphydrate solution was kept cold with ice and well shaken when the chloride was added. Potassium chloride separated. This was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in water and the solution acidified with hydrochloric acid. The product separated as an oil, but rapidly solidified, forming a red crystalline powder. This melted at 115°–116°.

Freshly prepared, it was readily soluble in chloroform or benzene, as well as in dilute ammonia and sodium hydroxide. Hydrochloric acid reprecipitated the thio acid from alkaline solutions. The substance, thus purified, melted at 116° with decomposition, leaving a yellow solid. The yield was 8.5 grams, or 85 per cent. of the calculated. The sample used for analysis was dried over sulphuric acid.

0.1969 gram substance gave 0.1171 gram $BaSO_4$.

	Calculated for $C_7H_5ONI_2S$.	Found.
S	7.90	8.16
N	3.45	3.38

The Disulphide of 2-Amino-3,5-diiodbenzoic Acid, $[C_6H_2NH_2I_2COS]_2$.—Attempts were made to purify the thio acid by concentrating a solution of the acid in chloroform on the steam bath. This treatment produced a yellow compound that decomposed at 202° and which would not dissolve in chloroform. The same effect was produced by heating in other solvents. When the thio acid was dried at 80° the compound which decomposed at 202° was also produced. This material did no dissolve in dilute ammonia or alkali. Owing to this property and since the same substance was obtained by treating the potassium salt of the thio acid with iodine, we conclude that the compound is a disulphide. One gram of the thio acid was dissolved in 20 cc. of water containing 0.14 gram of potassium hydroxide. To this solution 0.35 gram of iodine in 5 cc. of alcohol was then added. A yellow precipitate was immediately obtained. This decomposed at 202° and had all the properties of the compound obtained by heating the thio acid. It was almost insoluble in the common organic solvents. The portion analyzed was then obtained by dissolving the thio acid in chloroform and heating the solution.

0.1695 gram substance gave 0.1008 gram $BaSO_4$.

	Calculated for $C_{14}H_8O_2N_2I_4S_2$.	Found.
S	7.92	8.16

2-Amino-3,5-diiodbenzanilide was formed by the action of hot aniline on the disulphide described above. The disulphide at first dissolved in the excess of aniline, hydrogen sulphide was evolved and slender prisms separated from the solution. Alcohol was added and the residue filtered off. The product was almost insoluble in hot alcohol or water, and did not dissolve in 10 per cent. sodium hydroxide. It began to char slowly above 200° and melted to a black oil at about 224°.

	Calculated for $C_{13}H_{10}ON_2I_2$.	Found. I.	Found. II.
N	6.03	6.10	5.80

NEW HAVEN, CONN.,
February, 1910.

REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

XIII.—DERIVATIVES OF CYCLOHEXANE.

By E. P. Kohler and M. Cloyd Burnley.

It has been shown that many unsaturated ketones give both 1,2- and 1,4-addition products with organic magnesium compounds, and that the relative amounts of these products formed in any reaction depend on the nature of the magnesium compound as well as on that of the ketone. Most of the quantitative results published in previous papers were obtained by allowing a few organic magnesium compounds to react with a large number of typical α,β-unsaturated ketones. They show that the mode of addition to substances containing the chain C : C.C : O is influenced more by the number and spatial character of the hydrocarbon residues in combination with the chain than by the chemical character of these groups.

We have found it much more difficult to determine the relation between the mode of addition and the nature of the magnesium compound. A summary of the results hitherto obtained with different reagents is shown in the following table, which gives the percentage of 1,4-addition product obtained by treating benzalmethylethyl ketone with various magnesium compounds:

CH_3MgBr	70
C_2H_5MgBr	71
$C_2H_5CH(CH_3)MgBr$	69
$C_6H_5CH_2MgBr$	68
C_6H_5MgBr	40

These results led to the conjecture that the mode of addition to any given ketone depends more on the chemical than on the spatial character of the hydrocarbon residue contained in the magnesium compound.[1]

The results obtained with derivatives of cyclohexane support these conclusions. They show that while cyclohexyl-

[1] This Journal, **38**, 520.

magnesium bromide gives, with typical ketones, even more 1,4-addition product than the simplest aliphatic magnesium compounds, the cyclohexyl group in benzalmethylcyclohexyl ketone prevents 1,2-addition to carbonyl as effectively as does the phenyl group in benzalacetophenone or the isobutyl group in benzalpinacolin.

EXPERIMENTAL PART.

I. Experiments with Cyclohexylmagnesium Bromide.

In the first experiments we used cyclohexyl iodide, as this had been used by earlier experimenters because they obtained a much better yield of the iodide than of the corresponding bromide.[1] The ease with which the iodide yields free iodine, however, proved so objectionable in the quantitative separation of the products that we decided to try the bromide. We found that by a slight modification of the procedure recommended by Freundler and Damon[2] it is possible to get a yield of more than 95 per cent. of cyclohexyl bromide from cyclohexanol.

Our procedure was as follows: Cyclohexanol was allowed to drop, very slowly, into 15 per cent. more than the calculated quantity of phosphorus tribromide that was cooled in a freezing mixture. The liquid was constantly shaken and the temperature kept well below zero until all of the alcohol had been added. The resulting mixture was left in a freezing mixture for several hours, then placed in an ice chest overnight, and finally kept at the ordinary temperature for two days. The product, purified as directed by Freundler and Damon, gave 92–97 per cent. of the calculated amount of pure cyclohexyl bromide.

Cyclohexyl bromide reacts readily with magnesium suspended in absolute ether, but the quantity of active magnesium compound formed is much less than the calculated amount. A part of the bromide loses hydrogen bromide and passes into cyclohexene, while some more of it is condensed to dodecahydrodiphenyl. As it was essential to prevent the formation

[1] Ber. d. chem. Ges., **35**, 2688; **40**, 4168.
[2] Compt. Rend., **141**, 593.

of complex products by having a sufficient excess of magnesium compound, we based our calculations on the assumption that only 50 per cent. of the magnesium is transformed into active magnesium compound, although a series of tests with benzaldehyde showed 70 to 75 per cent.

The method used for determining the relative amounts of 1,2- and 1,4-addition products, formed in the reaction between the magnesium compound and ketones, was essentially the same as that described in an earlier paper. The mixture of substances left when the reaction was complete was poured into iced acid, the salts removed with water, and the ethereal solution dried and partially distilled under a pressure of 20 mm. The residue left after removing everything that distilled when the liquid was heated to 100° under this pressure still contained all of the 1,2- and 1,4-addition products, along with hydrocarbons and other impurities.

For the purpose of destroying the 1,2-addition product the entire residue was dissolved in acetone and treated with potassium permanganate. The complete removal of unsaturated compounds without oxidation of any of the 1,4-addition product proved somewhat difficult, because the precipitated oxides of manganese, in the state in which they were formed at the ordinary temperature, protected large quantities of oxidizable material. To avoid this difficulty we adopted the following procedure, which gave satisfactory results: The permanganate was added in small quantities to the cooled solution until the length of time taken for reduction showed that little oxidizable material was left in solution. The vessel was then connected with an inverted condenser, heated for 15 to 20 minutes at the boiling point of acetone, and cooled again to the ordinary temperature before more permanganate was added. By repeating this process 3 or 4 times it was possible to destroy all unsaturated compounds, in the course of 3 or 4 hours, without using an unduly large quantity of solvent.

The method of oxidation left the oxides of manganese in a form in which they were easily separated by filtration and

washed with acetone. The filtrate was concentrated by distillation, then fractioned under diminished pressure. It yielded a small quantity of hydrocarbons, then some indifferent substances resulting from the oxidation of the 1,2-addition product (as, for example, methylcyclohexyl ketone from the addition product with benzalacetone), and finally—boiling at a much higher temperature—the saturated ketone resulting from 1,4-addition. The weight of this fraction was used in calculating the amount of 1,4-addition.

Reaction with Benzalacetone: *Phenylcyclohexylbutanone*, $C_6H_5CH(C_6H_{11})CH_2COCH_3$.—The ketone is a solid that separates from alcohol in colorless needles melting at 67°. It is readily soluble in ether, chloroform, acetone, and boiling alcohol; moderately in cold alcohol and ligroin. The yield was 37.2 grams from 36.4 grams of benzalacetone.

Analysis:

0.2185 gram substance gave 0.6667 gram CO_2 and 0.1817 gram H_2O.

	Calculated for $C_{16}H_{22}O$.	Found.
C	83.43	83.21
H	9.56	9.24

Reaction with Anisalacetone: *Anisylcyclohexylbutanone*, $CH_3OC_6H_4CH(C_6H_{11})CH_2COCH_3$.—The ketone is a colorless, viscous liquid boiling at 218° (18 mm.). The yield was 44 grams from 42 grams of anisalacetone.

Analysis:

0.1666 gram substance gave 0.4767 gram CO_2 and 0.1817 gram H_2O.

	Calculated for $C_{17}H_{24}O_2$.	Found.
C	78.46	78.02
H	9.23	8.97

Reaction with Benzalethylmethyl Ketone: *Phenylcyclohexylpentanone*, $C_6H_5CH(C_6H_{11})CH_2COC_2H_5$.—The ketone closely resembles the product from benzalacetone. It crystallizes

in colorless needles melting at 71°. The yield was 43 grams from 40 grams of unsaturated ketone.

Analysis:

0.1420 gram substance gave 0.4337 gram CO_2 and 0.1289 gram H_2O.

	Calculated for $C_{17}H_{24}O$.	Found.
C	83.61	83.3
H	9.84	10.0

Reaction with Benzalacetophenone: *Phenylcyclohexylpropiophenone*, $C_6H_5CH(C_6H_{11})CH_2COC_6H_5$.—A large part of the ketone separated as a solid when the ethereal solution of the magnesium derivatives was poured into iced acid. The solid was redissolved with addition of ether, the ethereal solution dried, freed from ether, and treated with permanganate, as in previous cases. The entire product from 20.8 grams gave 0.5 gram of benzoic acid. This represents only 5 per cent. of the unsaturated ketone, leaving 95 per cent. to be accounted for as 1,4-addition product. The amount of saturated ketone isolated in pure condition was somewhat less than this, because the mixture of the ketone with hydrocarbons and indifferent oxidation products that was left after most of the ketone had crystallized defied quantitative separation.

Phenylcyclohexylpropiophenone is sparingly soluble in alcohol, ether, and cold acetone. It was recrystallized from boiling alcohol, from which it separated in needles melting at 122°–122°.5.

Analysis:

0.1878 gram substance gave 0.5957 gram CO_2 and 1.1413 gram H_2O.

	Calculated for $C_{21}H_{24}O$.	Found.
C	86.30	86.51
H	8.21	8.36

II. Experiments with Benzalmethylcyclohexyl Ketone.

Preparation.—The unsaturated ketone was made by condensing benzaldehyde with methylcyclohexyl ketone obtained

by substituting cyclohexyl bromide for the chloride in the method of preparation devised by Bouveault.[1] For the purpose of condensation 10 cc. of a 10 per cent. solution of sodium hydroxide was added to a solution of 10 grams of the ketone and 8.4 grams of benzaldehyde in 50 cc. of alcohol. The solution was shaken in ice water while the hydroxide was added and afterwards kept in an ice chest for 10–12 hours. The separation of solid was then made as complete as possible by cooling in a freezing mixture, the solvent removed with a pump, and the solid washed—first with well-cooled alcohol, then thoroughly with water—and recrystallized from alcohol. The best yield was about 80 per cent.

Analysis:

0.1813 gram substance gave 0.5592 gram CO_2 and 0.1328 gram H_2O.

	Calculated for $C_{10}H_{18}O$.	Found.
C	84.11	84.10
H	8.41	8.13

Benzalmethylcyclohexyl ketone, $C_6H_5CH : CHCOC_6H_{11}$, is readily soluble in all ordinary organic solvents except ligroin. It crystallizes in colorless plates that melt at 58°. Dissolved in carbon bisulphide, it rapidly combines with bromine and forms a solid dibromide melting at 139°.

Phenylbutylcyclohexyl Ketone, $C_2H_5CH(C_6H_5)CH_2COC_6H_{11}$.—Benzalmethylcyclohexyl ketone was added to ethereal ethylmagnesium bromide in the usual way. The product reduced only a trace of permanganate, showing that there had been no addition to carbonyl. Distillation under diminished pressure gave a very pale yellow liquid that boiled at 188° (16 mm.). The color was evidently due to a slight impurity that could not be removed by distillation but disappeared on very brief exposure to sunlight.

Analysis:

0.1820 gram substance gave 0.5594 gram CO_2 and 0.1580 gram H_2O.

[1] Centralb., **1903**, II, 1437.

	Calculated for $C_{17}H_{24}O$.	Found.
C	83.60	83.82
H	9.83	9.64

Diphenylethylcyclohexyl Ketone, $(C_6H_5)_2CHCH_2COC_6H_{11}$.—The product of the reaction between benzalmethylcyclohexyl ketone and phenylmagnesium bromide gave a trace of benzoic acid when treated with permanganate dissolved in acetone. It, therefore, may have contained a small quantity of unsaturated alcohol due to 1,2-addition. The saturated ketone formed by 1,4-addition boils at 250° (17 mm.) and melts at 68°. It is moderately soluble in alcohol and ether, readily in acetone. Its solution in alcohol deposits it in long colorless needles.

Analysis:

0.2056 gram substance gave 0.6500 gram CO_2 and 0.1468 gram H_2O.

	Calculated for $C_{23}H_{28}O$.	Found.
C	86.30	86.22
H	8.22	7.93

BRYN MAWR COLLEGE,
February, 1910.

AN EXTRACTION APPARATUS.

BY NORMAN ROBERTS.

The apparatus herein described consists of a battery of specially constructed extraction cells connected in series, together with an arrangement for evaporating, condensing and circulating volatile solvents. There are also described two varieties of supports designed for the convenient manipulation of long and otherwise unwieldy series of extraction cells. A search of catalogues and the literature shows no apparatus closely similar to this, and it has been thoroughly tried out in actual use and found to work well.[1]

[1] Ether extraction of corn meal in quantities of about 3 kg. per charge. The apparatus once started ran without attention, often without notice, for several hours. The loss of ether was slight, most of it being attributable to amateur construction of the apparatus.

Jackson and Clarke[1] have recently described an extraction apparatus for use with large amounts of solid substances, which, however, does not provide for the use of cells in series, and in which the percolate is obtained through a muslin-covered tube.

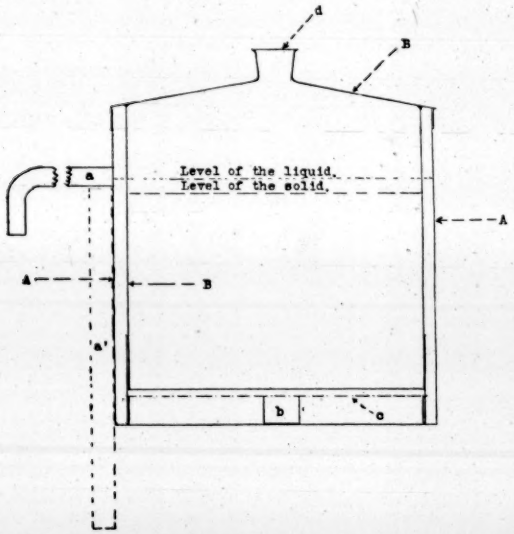


Fig. I.—The Individual Cell.

A, Outer container; B, inner container; a, overflow tube; a', position of overflow tube for vertical series; b, projecting leg at bottom of B; c, gauze bottom of B; d, mouth of B.

A number of ideas suggested themselves which we were not able to try in actual practice, as they required more mechanical skill and materials than were available. These untried ideas will be briefly described separately.

The individual extraction cell (Fig. I) is contructed as fol-

[1] THIS JOURNAL, **42**, 287–291 (1909).

lows: The outer container, *A*, is cylindrical, with an overflow tube *a*, a short distance below the top. The inner container, *B*, which also serves as a lid, is of such a size as to leave a narrow space betewen it and the outer container. The lower surface of *B* is of fine gauze, and is removable, being supported by a metal rim which fits tightly over the lower end of *B* like the lid of a can. To prevent accidental obstruction of the current by the falling or sagging of the gauze bottom, there are three short projections pointing downward, around the edge of the bottom. The upper surface of *B* (which serves also to close in the top of *A*) has a mouth by which it is connected to the adjoining part of the apparatus. The overflow tube *a* is set near the top of the container, being above the level of the solid and slightly below the level of the liquid in the inner container. The overflow tube is best made of glass, in order that the rate of flow may be watched.[1]

The evaporator may be a glass flask with suitable connections, heated by hot water, or it may be a flat metal vessel heated by steam or hot water in a drum underneath, and provided with a feed opening, an escape pipe for vapor, a draw-off cock, and a glass gage, closed at the top with a cork. In suitable cases, either electricity or a flame may be used as the heating agent. The condenser (best a glass Liebig), bridges the interval from the top of the vapor tube to the upper opening of the highest extraction cell. A glass adapter at this point enables one to see how fast the liquid is circulating, and a second adapter at the same point serves for the introduction of fresh liquid as required. The second adapter is closed by a cork carrying a long glass tube of small diameter and thin wall, surrounded by ice or cold water in a larger tube, which equalizes the pressure within and without, with a minimum loss by the escape of vapor; moreover, this cork, not being too tightly introduced, blows out in case of a sudden considerable

[1] In a large apparatus it would probably pay to have a cock at the bottom of the outer container, to drain it before cleaning out. In well constructed apparatus it would probably be feasible to free the exhausted solid from (volatile) solvents after draining, by blowing steam, best superheated, in a reverse direction, connecting the source of the steam to the overflow pipe, and the condenser to the mouth in the lid.

rise of pressure within. If the apparatus is well made, it should be possible to shut off the connection with the atmosphere entirely as soon as the apparatus is once fairly running.

The best materials are probably glass or tinned copper, each having its advantages and disadvantages. Inasmuch, however, as all parts of the extraction cell are accessible on

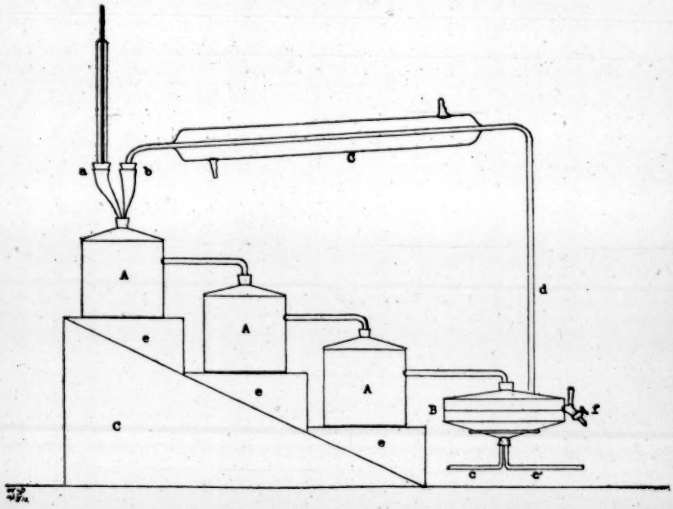


Fig. II.—Complete Apparatus (Oblique Form, with Support).

A, exterior cells; B, evaporator, lower half being the steam jacket; C, oblique support; a, adapter, with capillary tube, jacketed; b, adapter, from condenser; c, c', steam inlet and exhaust pipes; d, vapor tube from evaporator; e, sliding supports for cells; f, drain cock and gage.

both sides for cleaning and drying, tinned iron may be used without much fear of rusting if reasonable care be taken.

Operation.—It will be noted that the apparatus contains no filtering or straining layer—no cotton packing, sand, etc. The single layer of gauze serves merely to keep the *mass* of

powder in place, clarification being effected by sedimentation as the percolate slowly rises in the space between the inner and outer containers. Filtration, if ever necessary, is best done outside of the cell. Owing to the absence of passive obstruction, all the excess of liquid in the apparatus accumulates in the lowest part of the circuit, namely, in the evaporator, and the rapidity of the circulation is dependent entirely on the rate at which heat is applied to evaporate the solvent. Freshly charged cells are introduced at the lower end of the series. Charging a cell of this kind is a much simpler matter than charging an ordinary percolator, as no special packing or great amount of skill is required. If the powder does not swell on wetting, it is charged dry; if it does swell, it is given an opportunity to do so before being charged. In charging, the inner container is inverted, the gauze bottom removed, the proper amount of powder introduced (it must be entirely submerged during extraction), the gauze replaced, and the whole (inner container) allowed to settle slowly into the proper amount of liquid previously introduced into the outer container. It is often advantageous to combine maceration with percolation, by alternately circulating the solvent and letting it rest, which can be done, *e. g.*, by turning the heat and water to the condenser on during the day, and off during the night, or during other proper intervals.[1]

It is, of course, possible to use a single extraction cell only, but a series, even of two, is far preferable, by reason of increased rapidity and completeness of extraction. Too long a series necessitates the use of too much liquid (especially, for example, of ether) and is unwieldy and labor-consuming; but under suitable conditions (as when the percolate cannot be heated), a long series gives ideal results, especially as to saturation and therefore uniformity of percolate and the exhaustion of the powder or other matter being extracted.

A lute of glycerol and kaolin is of great service in extraction with ether.

[1] It is possible, but rather dangerous, to leave this *or similar apparatus* running all night. When no one is within hearing distance, it is preferable to trust to the slower but safer process of maceration in any extraction with volatile and inflammable solvents.

The Support.—Probably the chief reason for the unpopularity of long-series percolation on the small scale is the trouble of changing the cells. Unless all joints are *perfectly* tight (a difficult condition), pressure, as a means of circulating the liquid, is out of the question, and gravity must be relied on. This necessitates a step- or ladderlike support, with a stepping up of each cell and its disconnection and reconnection to both of its neighbors. With only two or three cells in series, this is little extra trouble, but the work soon becomes prohibitive as the number of cells in series increases. But by the use of sliding supports the series can be moved up *en masse* when the top cell is to be removed and a fresh cell introduced at the bottom. The guide on which the supports slide may be vertical or inclined; in either case, a separate sliding base will be needed for each cell. In the vertical form the guide is a rod (gas pipe), the sliding bases being L-shaped wooden pieces, the vertical limbs of which slide on the guide, which fits in a deep groove and is held on by a catch, while the horizontal limb supports the cell. In the oblique form the guide is an inclined plane, and the sliding bases are steplike platforms. The vertical form needs little desk room, and is convenient for small cells in not too long series. The oblique form would seem to be useful for long series of large cells. I have tried the vertical form with good results. The oblique form is as yet only on paper, since I have never worked with large cells in series of more than two.

The following suggestions are due to my assistant, Mr. F. Alex. McDermott, who has helped make the apparatus and has done most of the work of operating it:

Where the most rapid and efficient working is desired it is best to have at least one more cell than the number required to make up the battery. The extra cell or cells stand charged and macerate while the battery is percolating, each cell being cleaned and recharged as soon as it is removed exhausted from the upper end of the battery. When a fresh cell is needed, the cell which has stood macerating longest is connected in at the bottom, and the exhausted cell at the top removed,

and percolation is thus continued with the minimum of interruption.

If the apparatus is constructed of metal, it is desirable to use the same metal throughout, to avoid possible electrolytic effects.

The heat applied to the evaporator should be as constant as possible; sudden accessions of heat (absolute or relative) cause corresponding increases of pressure in the system; if extreme, this phenomenon may be practically an explosion. This is one reason (probably the best) for turning off the heat at night or at other times when the apparatus cannot be watched.

DIVISION OF CHEMISTRY, HYGIENIC LABORATORY U. S. PUBLIC HEALTH AND MARINE HOSPITAL SERVICE, WASHINGTON, D. C.

NOTE ON THE REACTIONS OF DIAZOALKYLS WITH 1-PHENYL-2-METHYLURAZOLE.

BY SIDNEY NIRDLINGER, E. K. MARSHALL, JR., AND S. F. ACREE.

In the article in the April number of THIS JOURNAL,[1] $\frac{K_{trans}}{K'_{trans}}$, line 11, p. 361, should be $\frac{C_2}{C_3}$. This oversight does not occur in the fuller discussion in the succeeding pages.

On p. 367 it is not stated that the experiments by Mr. Marshall with diazoalkyls were *not* performed at 25°; as stated on p. 363, line 8, his work is being done at *lower* temperatures, 0° and —70° at present. Under these conditions only does the ratio of esters obtained when the acid is freshly liberated from the salt differ at all from that found when the acid is allowed to change with time. Whether this change is due to a rearrangement of two or more tautomeric forms, as we believe, or to slow ionic changes, salt formation, polymerization, etc., is being investigated. It may be mentioned here that Mr. Marshall finds that the ratios, *N*-ester : *O*-ester, obtained from the silver salt of 1-phenyl-2-methylurazole

[1] Vol. **43**, p. 358.

and methyl iodide in 40 per cent. alcohol are approximately the same, whether the silver salt be *suspended* or *dissolved*.

Mr. Marshall has further found that the ratios *N*-ester : *O*-ester, obtained from the sodium, zinc and silver salts at —70°, when the 1-phenyl-2-methylurazole is liberated by hydrochloric acid from the salts in alcoholic-ether solutions in the presence of diazomethane, are all practically the same, about 87 : 13. The 1-phenyl-2-methylurazole in alcoholic ether solutions at 20°, 0°, or —70° gives a ratio 94 : 6. This shows that these salts all have about the same equilibrium constants, which are slightly different from those for the acid. The mass law requires that the ratios of keto to enol ions be the same for all salts and the acid in dilute solutions. Whether this difference between the equilibrium constants for the acid and for the salts is due to a difference in the dissociation constants, and to a difference in the ratio of molecular keto and enol forms, or to an apparent change in the ratio of the keto and enol ions because the ordinary dilution formulas do not hold in the rather concentrated solutions used, or to other causes, is being investigated. We have made the very important observation that the silver salt has apparently about the same equilibrium constants as the other salts. The higher percentage of *O*-ester which we have obtained from the silver, mercury and lead salts and alkyl halides may be, to some extent, due to *a reaction of the undissociated*[1] *salt, which we have several times discussed as possible*, or to other causes. Mr. Marshall is investigating this subject fully.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, April 8, 1910.

OBITUARY.

HANS LANDOLT.

With the passing away, on March 15th, of Landolt, nearly the last of the old school of physical chemists is gone. This school had for its aim the study of the physical properties of chemical compounds. The members of this school, of

[1] THIS JOURNAL, **38**, 260–1; Ber. d. chem. Ges., **41**, 3210, 3214, etc.

whom we need mention only Gladstone and Perkin in England, and Kopp and Landolt in Germany, lived in that period when chemical compounds were made by the thousand. This applies especially to organic compounds, the incentive being for a long time the fertile theory of Kekulé.

As these compounds were brought to light, it became desirable to know their physical properties, and these were studied with a degree of thoroughness and comprehensiveness which must always arouse the admiration of men of science. Take, for example, the work of Kopp on the boiling points of liquids, of Perkin on magnetic rotation, and of Landolt on refractivity, optical activity, etc.

Hans Landolt was born December 5th, 1831, in Zurich. His earliest work in chemistry was done at the University of Zurich under Loewig. When the latter was called to Breslau young Landolt followed him there and obtained from this institution the degree of Doctor of Philosophy in 1853, his dissertation being upon "Arsenic Ethyl."

From Breslau, Landolt went to Berlin to study with Rose and Mitscherlich, and then to Heidelberg, to work with Bunsen. He returned to Breslau in 1856 as privatdozent, and in 1867 was appointed full professor in Bonn. Two years later he accepted the professorship of chemistry and mining at the Technical High School in Aix-la-Chapelle. In 1880 Landolt accepted the professorship at the newly opened Agricultural High School in Berlin, and in 1891 succeeded Rammelsberg as director of the II Chemical Institute at the University of Berlin. This position he held until he retired in 1905.

The most important lines of work with which the name of Landolt will always be connected are the following:

From his study of the molecular refraction of organic compounds he arrived at the formula connecting the index of refraction with density, which is the simplest and the best expression of this relation, even at the present time.

One of his best known investigations is in connection with the optical activity of organic compounds. He made

an exhaustive study of the effect of the solvent, of the temperature, etc., on this property, and greatly improved the apparatus used in measuring optical rotation. His book dealing with optical activity, "Optisches Drehungsvermögen organischer Substanzen und dessen praktische Anwendungen," is *the* authority in this field. Landolt's work on the melting points of organic compounds is not as well known as those lines of investigation referred to above, but shows that love of accuracy which characterized everything that he did.

The investigation for which Landolt is best known to the younger generation of physical chemists, or the so-called new school of physical chemists, is that which has to do with the fundamental question whether the law of the conservation of mass holds rigidly when chemical reactions take place? The question to be answered experimentally was whether weight remains constant during chemical reaction. Do the products of a chemical reaction weigh the same as the substances that entered into the reaction?

The writer had the good fortune to see in progress, in 1893, this work which was carried on for nearly twenty years.

The first part of the problem was to secure a fine balance, and Landolt had constructed for this work the finest chemical balance that the world had ever seen. This was but the beginning. Every possible precaution against changes in temperature, mechanical disturbance, and the thousand and one other disturbing effects was adopted and with such skill, that this investigation alone places Landolt in the very first rank of careful workers.

At first Landolt found changes in weight that were larger than could be accounted for by experimental errors. He, however, continued this very exacting investigation even after he retired from active professional work, and lived to furnish a perfectly satisfactory explanation of the changes in weight that he had found. They were due to changes in the volume of the vessels containing the reacting substances, caused by small changes in temperature.

By the death of Landolt chemistry loses one of her most careful investigators, and those who knew him lose a kind-hearted, generous and sympathetic friend—a man who lived for a scientific ideal. H. C. J.

REPORTS.

INDUSTRY AND ANALYSIS OF THE FATS.[1]

The chemistry and modern industry of the fats originated in France. It is, in fact, on the shores of the Mediterranean that the cradle of the discovery of soap and, consequently, of saponification, the fundamental operation in the chemistry of the fats, must be sought. Whether the Arabs, who, thanks to the discovery of the chemical action of quicklime on the ashes of saliferous plants, knew how to prepare a hard soap from olive oil, taught this art to the people of Marseilles, or whether the latter learned it from the Genoans, it is a well-established fact that in the 11th century the art of the soap maker enjoyed a high reputation at Marseilles and reached such a degree of perfection that for several centuries "Marseilles soap" held the first rank among all the world's soaps.

The lure of gain having soon led to fraud by the introduction into soap of an excessive quantity of water, a practice which analysis alone could expose, the detection of fraud by means of chemical analysis became necessary. The analysis of soap originated in France as early as the 18th century and it was Claude Joseph Geoffroy who, probably in the course of such an analysis, made the important observation that the fatty substance separated from soap by the action of hydrochloric acid was clearly distinguished from natural fats by the ease with which it dissolved in alcohol. It appears that his contemporaries were in no wise ignorant of this observation. Three years later, in 1745, Macquer recognized that the greater solubility in alcohol of rancid fats is due to the presence of an acid substance, and he found that the solubility increased directly as the quantity of free fatty acids.

The discovery of fatty acids was thus made. As seen from the point of view of our present knowledge, the discovery of glycerol by Scheele, in 1783, ought to have furnished the key to the constitution of the fats, but the science of chemistry was not yet sufficiently advanced. Scheele regarded the fats as compounds of carbonic acid, water, and phlogiston.

[1] Address delivered before the Société Chimique de France, April 3, 1909, and published in Bull. Soc. Chim. of May 20, 1909.

The solution of the problem was reserved for the genius of Chevreul who brought light and cleared up the darkness in which the chemistry of the fats was then buried. The immortal researches of Chevreul, the establishment of the industry of the fatty acids which immediately resulted from them, and the brilliant succession of investigations by Berthelot and by Wurtz, who confirmed, consolidated, and elaborated the views of the master, are too well known by every one to need being traced again in this rapid retrospective review.

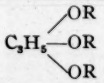
It is therefore rather the modern development of the chemistry and industry of the fats, the exposition of which the Council of the Société Chimique has been kind enough to confide to my feeble efforts, which will take up our attention today.

It had, to be sure, been recognized that the natural fats consist exclusively of triglycerides; the mono- and diglycerides, whose properties had been made known through the beautiful syntheses of Berthelot, had not been found in natural fats. The only apparent exception to this general rule, furnished by the presence of dierucin in some old oils of colza, is easily explained, as we shall see later, by the fact that the oils had become rancid.

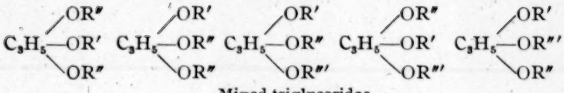
The various known fatty acids must give rise to as many different triglycerides, resulting from the combination of a molecule of glycerol with three identical acid radicals. We shall call them *simple glycerides*.

The number of simple glycerides being limited by the number of known fatty acids, chemists could not, for a long time, explain the differences exhibited by fats and oils apparently containing the same fatty acids otherwise than by assuming varying proportions of the corresponding triglycerides. Berthelot, nevertheless, had, as early as 1860, expressed the opinion that the complexity of the natural fats might be explained by the existence of compounds in which one molecule of glycerol was combined with the radicals of two or three different acids. Glycerides of such a composition would be called *mixed glycerides*.

To make clear the ideas on this point, it is well to bring together the different possible combinations in the following scheme:



Simple triglyceride.



Mixed triglycerides.

Although quite a large number of simple triglycerides were known in pure state—tributyrin having been prepared as early as 1844 by Pelouze and Gélis—it is only within the last ten years that it has been possible to extract from a natural fat a true mixed triglyceride. Oleodistearin, discovered by Heise, opened the series; there then followed, in perhaps too rapid succession, palmitodistearin, stearodipalmitin, myristo-palmito-olein, dipalmito-olein, and dioleostearin (whose existence is still doubtful), and a few other mixed glycerides, put forward as chemical individuals but to-day abandoned as not existing.

The difficulty of isolating such chemical individuals in pure state is considerable; this is perhaps due to the intramolecular changes which mixed glycerides suffer during the treatment with solvents. But the conviction that mixed glycerides form the larger proportion of the natural fats will be borne upon us when we recall the laborious experiments of Bömer, according to whom beef and mutton tallow contain no more than 1.5 to 3 per cent. of tristearin, a result demonstrated by a very large number of crystallizations from various solvents.

Thanks to the elaboration of Berthelot's classical methods, much work has been done in the preparation of mixed glycerides. To-day more than a score are known, the simplest of which is acetodiformin, prepared by Béhal. From the formulas given above, it follows that with two different acid radicals two isomers are possible, and that if all three acid radicals are different three isomers can exist. When the number of known fatty acids is considered, it will easily be seen that the number of different triglycerides whose existence in natural fats is possible must be enormous. In order to calculate their number, Berthelot gave formulas which Kablukow has developed; but although indicating an extraordinary number, amounting to thousands, of possible combinations, these formulas do not represent all the isomers predicted by the theory. Let oleic acid be replaced by its isomer, elaidic acid, or erucic acid by brassidic acid, and the number of mixed glycerides containing these acids will be doubled and quadrupled. Assume racemic combinations such as those repre-

sented by the last four formulas, let these be split up into two opposite optical isomers—without prejudice, however, to the optical activity due to the acid radicals themselves—and the number of mixed glycerides will again be doubled. We shall not expatiate on this prodigious multiplicity and shall not even try to evaluate it. We have as yet reached only the preliminary stage in the work leading to the clear resolution of the different glycerides which constitute any one oil or fat.

It might be thought that one means which, if not quite simple, could at least be used for determining the composition of these apparently irresolvable mixtures, would consist in extracting from them, by repeated crystallizations, individ uals whose properties could be compared with those of compounds prepared synthetically; recourse would then be had to elementary analysis. But such is not the case, for the differences between the percentages of carbon, hydrogen, and oxygen are too small to furnish useful indications. We might perhaps turn to the melting point, a constant so characteristic for pure organic substances. Unfortunately, the mixed glycerides present the phenomenon of double melting point in a manner even more deceptive than the simple glycerides. Abandoning the hypothesis of the existence of two modifications, pointed out some fifty years ago by Duffy and by Heintz, it was sought to explain this curious property by the phenomenon of superfusion of the melted substance cooled below its freezing point and not yet returned to its normal crystalline state. The original hypothesis has recently acquired new life, thanks to the almost simultaneous, independent investigations of Grün and Schacht and of Bömer. The experiments of these authors have shown that the mixed glycerides can be obtained in two forms, *viz.*, an unstable and a stable modification. By inoculating the unstable fat with a crystal of the stable modification, the former is gradually converted into the stable form, characterized by a melting point higher than that of the unstable modification. The latter has the lower melting point, called the "first melting point," or, following Bömer's suggestion, the "transition point." The compounds obtained in crystalline form have but a single melting point, the higher. It is the modification which cannot be converted into its unstable isomer by the inoculation method. The "true melting point" should therefore be assigned to the crystalline forms. It is at all events certain that there exist two forms, but the cause of this cannot yet be explained. Is the existence of these two forms due

to a polymerization? The determination of their molecular weights by the freezing and boiling point methods has furnished no decisive indications on this subject. Perhaps the unstable modification is one of those liquid, anisotropic phases described by Wallerant and Jaeger, a hypothesis which becomes more probable when we consider the fact that the melting points vary irregularly when the substances are allowed to stand for longer or shorter periods of time. Here are phenomena which offer a vast field for investigation and, consequently, for discoveries. Without exaggeration, it can be said that there is enough work here for a whole army of investigators.

We shall confine ourselves here to the consideration of the mixed glycerides containing three organic acid radicals. Mixed glycerides with organic and mineral acid radicals are beyond the scope of our study. But it is meet to consider briefly, in passing, a very remarkable mixed glyceride containing the radicals of phosphoric acid and of two fatty acids; I refer to lecithin, a natural principle found in the yolk of eggs, milk, the retina of animals of the bovine genus, the grains of maize, peas, the gluten of wheat; in sum, a fat seeming to play an important rôle, still ill defined, in the economy of the animal and vegetable organism. We see here an important point of contact between the pure and applied chemistry of the fats and their physiological chemistry.

Moreover, we shall return to this point frequently in the course of this address.

We know that the most important chemical reaction of the fats is saponification, or, in scientific language, hydrolysis.

The splitting up of the glycerides into glycerol and fatty acids is not a tetramolecular reaction such as treatises on general chemistry represent by the equation

$$C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix} + 3H{-}OH = C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix} + 3R{-}OH.$$

It takes place in three consecutive phases, which may be represented by the three following equations:

$$(1a)\quad C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix} + H{-}OH = C_3H_5\begin{matrix}OH\\OR\\OR\end{matrix} + R{-}OH;$$

$$(1b)\quad C_3H_5\begin{matrix}OH\\OR\\OR\end{matrix} + H{-}OH = C_3H_5\begin{matrix}OH\\OH\\OR\end{matrix} + R{-}OH;$$

$$(1c)\quad C_3H_5\begin{matrix}OH\\OH\\OR\end{matrix} + H{-}OH = C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix} + R{-}OH.$$

From the triglycerides we pass to the diglycerides, then to the monoglycerides, ending up finally with the products of complete hydrolysis. This way of looking at the fundamental reaction in the chemistry of the fats has been criticized by several chemists, but it has been verified by numerous experiments, purely chemical as well as physico-chemical. It has been shown in an almost irrefutable manner that hydrolysis takes place in three phases. Thanks to this agreement between the chemical and physical evidence, the general equation,

$$C_3H_5(OR)_3 + 3H{-}OH = C_3H_5(OH)_3 + 3R{-}OH,$$

must be considered as the resultant of the three equations given above, each of the latter representing a bimolecular reaction.

It cannot be expected that these three phases should succeed each other consecutively in an absolutely distinct manner, nor can it be hoped to find the total mass of the triglycerides at first completely and exclusively decomposed and transformed into diglycerides according to equation (1*a*), then this mass of diglycerides transformed completely into monoglycerides according to (1*b*), and lastly the monoglycerides finally split up into glycerol and free fatty acids. We must rather expect to find the three phases represented in the equations above taking place simultaneously and concurrently, so that at the same moment one molecule of diglyceride may be transformed into a monoglyceride and a fatty acid, one molecule of monoglyceride be decomposed into glycerol and a fatty acid, while one molecule of triglyceride may still remain intact or undergo the first phase.

Hydrolysis does not take place in the absence of water. The latter must therefore be considered as the hydrolyzing agent, whether it be used alone or with catalytic agents, such as bases, acids, or enzymes.

At ordinary temperatures water alone acts extremely slowly on glycerides; in fact, at ordinary temperature, in the absence of favorable conditions (such as the simultaneous presence of light and of atmospheric oxygen), the hydrolysis would be almost *nil*. It will be recalled that Friedel found unchanged triglycerides in fats from the tombs of Abydos, the existence of which goes back several thousands of years. But let the temperature of the water be raised to 220°, and almost complete hydrolysis will be effected. That is the principle of the Tilghmann process, perfected by Hughes, which has been put into operation on an industrial scale in one of the stearin factories of Paris.

The saponification by caustic potash and soda had been carried on for centuries, but it had never been recognized that this operation consists of two clearly distinct chemical reactions. First phenomenon: hydrolysis of the fat, the alkali acting only as an accelerator or catalytic agent. Second phenomenon: formation of soaps by the union of the fatty acids with the alkali. The alkali always being present in excess, the two reactions take place almost concurrently and were regarded as consisting of but a single reaction. It is only since the creation of the industry of the fatty acids that the clear distinction between the two consecutive phases has become well understood by the soapmaker.

If we admit as being correct the point of view that the caustic alkalies are accelerating or catalytic agents, it follows that it is not necessary to use at least molecular proportions of these bases relatively to the fatty acids set free by complete hydrolysis. The greater the proportion of bases present (allowance being made for the chemical affinity or the accelerating power of the different bases), the more rapidly must the hydrolytic resolution of the glycerides be effected and the greater must be the quantity of salts of fatty acids formed. But the use of a quantity of bases smaller than would be necessary to neutralize the fatty acids produced by complete hydrolysis ought not to prevent the decomposition into glycerol and fatty acids from being completely effected. This, evidently, is not the process employed industrially with the caustic alkalies; but there is no doubt that, under pressure, complete hydrolysis could be effected with a proportion of alkali insufficient to neutralize the fatty acids formed.

Let us verify the correctness of our views by studying the saponification of fats by quicklime: The theoretical quantity of caustic lime necessary for the saponification of a fat whose mean molecular weight is 860 is 9.7 per cent.

Unless the proportion of lime is increased to 12–14 per cent., complete hydrolysis of the fat cannot be effected in an open vessel, *i. e.*, under atmospheric pressure and at a temperature of 100°–105°. But let the pressure be raised to 12 atmospheres, which corresponds to a temperature of about 190°, and 1 per cent. of lime will be sufficient to effect practically complete hydrolysis. This quantity of lime is converted into a calcium soap by a subsequent reaction. We should lay stress on this fact, that in using lime as an accelerator we have lowered considerably the temperature necessary for complete hydrolysis by means of water alone. Magnesia and zinc oxide behave like lime.

Thanks to the investigations of Chevreul and of Fremy, it had been recognized that concentrated sulphuric acid can likewise effect complete hydrolysis of fats. We prefer to say that sulphuric acid behaves like a catalytic or accelerating agent. If a fat is heated at 120° with 4 per cent. of concentrated sulphuric acid and the mass is kept stirred by a current of steam, hydrolysis is effected in about ten hours. This is shown in the following table:

Table I.—Tallow Hydrolyzed at 120° with 4 Per Cent. of Sulphuric Acid (Lewkowitsch.)

Sample taken after	Free fatty acids. Per cent.	Sample taken after	Free fatty acids. Per cent.
1 hour	42.1	6 hours	91.7
2 hours	65.1	7 "	91.7
3 "	79.3	8 "	92.3
4 "	83.7	9 "	93.0
5 "	88.6		

The sulphuric acid acts in the first place through the formation of sulphonated compounds of the glycerides, forming a perfect emulsion with water and thus favoring the intimate contact between the hydrolyzing water and the globules of the nonsulphonated fats which are divided, pulverized, so to speak, by the steam. The accelerating action of the acid would thus be explained. On the other hand, dilute sulphuric acid, not being able to form sulphonated compounds, ought not to act as a catalytic agent, and hydrolysis should decrease progressively as the concentration of the sulphuric acid diminishes. This is quite in harmony with the facts, as is shown in Table II.

Table II.—Hydrolysis of Tallow Containing 6.2 Per Cent. Free Fatty Acids with 4 Per Cent. of Sulphuric Acid of Different Concentrations (Lewkowitsch).

Per cent. H_2SO_4 in acid.	Per cent. of fatty acids after action of steam for *T* hours.										
	T = 1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
98	42.1	65.1	79.3	83.7	88.6	91.7	91.7	92.3	93.0	92.3	93.0
90	37.2	47.7	57.6	65.1	72.5	76.0	80.0	81.8	83.6	86.2	88.0
85	34.1	45.2	50.8	62.6	68.2	73.1	75.0	76.2	79.4	84.3	84.9
80	31.6	45.2	57.6	65.1	73.1	75.4	79.3	80.6	83.7	85.5	87.4
70	15.5	16.7	17.9	18.3	18.6	20.3	24.8	26.5	28.5	31.0	32.6
60	6.2	6.2	6.2	6.2	....	....	....	....	....	....	....
50	6.2	6.2	6.2	6.2	6.8	....	....	....	....	....	....
	T = 12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.
98	93.6	93.6	93.0	93.6	93.6	....	....	....	....	....	....
90	86.8	88.6	88.6	89.0	90.5	90.5	....	....	....	....	....
85	89.3	89.3	89.3	89.9	89.9	89.9	....	....	....	....	....
80	88.6	89.0	89.9	89.9	89.9	42.7	....	....	....	....	....
70	34.7	35.4	37.0	39.0	40.1	42.7	45.2	46.5	47.7	47.7	47.7

Table III.—Hydrolysis of Oils and Fats with Twitchell's Reagent (Lewkowitsch).

(100 grams of oil or fat subjected to the action of steam with 1 per cent. of sulpho aromatic compounds in open vessels.)

Oil or fat.	Original acid number.	Acid number after T hours.							
		$T=2$.	7.	9.	12.	14.	16.	18.	20.
Cotton	5.67	8.75	61.28	99.8	129.4	137.6	148.7	150.1	155.9
Whale	6.01	14.99	48.69	63.72	72.42	80.8	84.31	85.82	89.68
Colza	2.16	8.4	23.24	30.59	44.26	50.57	53.6	55.4	56.58
Lard	2.6	1.37	38.66	58.73	82.42	90.81	98.49	107.3	107.9
Tallow	11.15	5.03	25.68	43.44	49.39	50.11	52.03	53.1	53.85
Cocoa	18.75	114.0	221.4	232.9	233.2	236.0	236.2	237.2	237.9

	$T=22$.	24.	26.	28.	30.	32.	34.	36.
Cotton	157.9	161.4	164.5	165.2	166.3	167.0	168.4	168.9
Whale	90.71	91.67	91.67	91.7	94.69	97.88	98.07	98.9
Colza	56.72	57.91	59.58	60.6	61.46	61.61	61.87	62.3
Lard	109.0	110.5	112.0	115.2	118.3	118.6	119.1	120.2
Tallow	55.6	57.11	59.82	60.23	63.95	66.2	67.3	68.5
Cocoa	238.9	239.5	239.8	239.8	240.6	240.9	241.0	241.2

We see that, beginning with 60 per cent. sulphuric acid, hydrolysis ceases completely.

The chemical action which sulphuric acid exerts on unsaturated acids is, moreover, not contrary to our views; it is a secondary reaction comparable to the formation of a calcium soap in the process of water hydrolysis accelerated by lime.

This is shown clearly by the action of Twitchell's reagent, a sulphostearo aromatic compound obtained by the action of concentrated sulphuric acid on a mixture of oleic acid and aromatic hydrocarbons, such as benzene or naphthalene.

One to 2.5 per cent. of this reagent is sufficient to effect, in a given time, almost complete hydrolysis of fats heated in a current of steam at ordinary pressure, especially in the presence of a few per cent. of free fatty acids.

In Table III are given the results of a series of experiments carried out in the laboratory with a commercial reagent.

Experiments carried out with reagents prepared from naphthalene, anthracene, and phenanthrene, are summarized in Table IV:

Table IV.—Hydrolysis of Cotton Oil with 1 Per Cent. of Sulphostearo Aromatic Compounds (Lewkowitsch).

(*a*) Neutral oils.

Compound with	Original acid number.	6.5 h.	13 h.	19.5 h.	26 h.	32.5 h.	39 h.	45.5 h.
Naphthalene	1.22	146.7	190.7	201.4	211.4	...	...	...
Anthracene	1.22	2.5	21.8	76.3	170.7	186.5	190.7	...
Phenanthrene	1.22	45.7	125.7	177.7	183.6	194.1	201.2	...

(*b*) Oils containing free fatty acids.

Naphthalene	8.3	30.9	194.1	216.9	210.7	...	...	...
Anthracene	8.3	15.01	60.5	112.4	147.2	148.2	189.8	202.8
Phenanthrene	8.3	42.3	159.9	156.4	181.6	184.2	204.2	204.2

These reagents in no wise react on the unsaturated acids of a fat. We must therefore attribute their accelerating power to their emulsifying action, which facilitates the hydrolysis of the fat globules in intimate contact with the water molecules.

Stress should be laid on this important fact, that no secondary reaction seems to intervene, the fatty acids obtained by this method being the unchanged hydrates of the acid radicals which were combined with the glycerol in the nonhydrolyzed fats.

It seemed to us that hydrochloric acid might serve to show even more clearly that the hydrolyzing action of water is simply accelerated by catalytic agents, the hydrochloric acid taking no part in the chemical reaction. Our experiments on this point are given in Table V:

Table V.—Hydrolysis of Oils and Fats with Hydrochloric Acid of Specific Gravity 1.16.

(100 grams of fat boiled with 100 cc. of acid.)

Oil or fat.	Original acid number.	After 24 hours.	Acid number of completely hydrolyzed fat.
Cotton	0.35	143.9	202
Whale	6.01	157.3	195
Colza	2.16	131.7	185
Lard	1.25	140.3	201
Tallow	11.15	150.0	200
Cocoa (copra)	18.75	204.9	260
Castor	1.22	49.14	190

A certain amount of hydrochloric acid having escaped in the gaseous state in these experiments, in the experiments given in Table VI a fresh addition of hydrochloric acid was made after taking each sample:

Table VI.—Hydrolysis of Oils and Fats with Hydrochloric Acid of Specific Gravity 1.16.

(100 grams of oil or fat and 100 cc. of acid; acid added after taking each sample.)

Oil or fat.	Original acid number.	Acid number after T hours.				
		$T = 2$.	7.	9.	12.	14.
Cotton	0.35	18.42	79.6	95.51	116.2	136.4
Whale	6.01	26.69	101.3	120.3	142.7	155.4
Colza	2.16	19.66	75.06	89.57	107.2	120.1
Lard	1.25	14.51	84.78	116.8	139.8	149.4
Tallow	11.15	43.39	112.5	131.7	153.2	167.0
Cocoa	18.75	79.73	184.2	210.5	221.4	230.8
Castor	1.22	44.4	47.3	49.0	51.4	51.4

Table VI—(Continued.)

	Acid number after T hours.					Acid number completely hydrolyzed fat.
	T = 16.	18.	20.	22.	24.	
Cotton	144.9	155.7	164.8	168.2	175.8	202
Whale	162.3	170.0	172.0	...	...	195
Colza	127.3	134.2	140.3	144.0	151.8	185
Lard	152.1	162.7	168.0	173.0	177.0	201
Tallow	173.3	178.9	183.3	185.2	186.8	200
Cocoa	233.4	239.8	241.1	246.1	250.1	260
Castor	47.9	49.2	46.8	44.4	41.64	190

In other experiments (published elsewhere) carried out for the purpose of accelerating still more, if possible, the catalytic action of hydrochloric acid, it was not found possible to obtain complete hydrolysis. In fact, the reaction slows up very much when the hydrolysis reaches 75 per cent. It is difficult to maintain, during the experiments, an intimate mixture of the fats and dilute acid; this might explain the slowing up of the reaction. By realizing a perfect mixture, such as an emulsion, it might be hoped to obtain complete hydrolysis, for the catalytic action of hydrochloric acid manifests itself, with time, even at ordinary temperature. Thus, cotton oil mixed with hydrochloric acid is hydrolyzed 75 per cent. after 213 days' contact.

We thus approach, step by step, the methods which Nature applies *in vivo*. The oleaginous seeds contain considerable quantities of fats, which have accumulated in them, to serve as nourishment for the embryo. How is this transformation brought about? It is certain that it begins by the hydrolysis of the fats, for Pelouze showed in 1855 that the seeds of the flax, the poppy, the camelina, the colza, peanuts, sweet and bitter almonds, contained a principle, then unknown, capable of effecting quite rapidly the hydrolysis of the oils in the seeds. Then the experiments of Müntz, in 1871, established the fact that the first phase in the utilization of the fats accumulated in the seeds takes place concurrently with the hydrolysis of the fats and that the observed acidity is due to the fatty acids liberated from the neutral glycerides.

This is a very important observation, which was, moreover, confirmed by Schützenberger in 1876. From that time date the attempts made to isolate the hydrolyzing principle. Maillot, in 1880, found in the castor bean a soluble ferment to which he attributed the lipolytic power. This fact was confirmed by Green and by Sigmund. Finally, thanks to the work of Connstein and his collaborators and to the ex-

tended investigations of Nicloux, these operations passed from the domain of the laboratory to that of industry.

Nicloux's cytoplasm, *i. e.*, the soluble ferment of his predecessors, behaves like a catalytic agent, obeying the physicochemical laws which govern the speed of hydrolysis. Mixed with oil in the presence of water acidulated with a minimum quantity of a suitable acid or acid salt, cytoplasm effects the hydrolysis of fats *in vitro*.

It is the same phenomenon which is realized in cellular life during the germination of the oleaginous seed! Can we therefore put forward the view that all seeds containing fats in reserve for the nourishment of the embryo enclose at the same time an enzyme or cytoplasm or soluble ferment which, thanks to the water and carbonic acid always present in sufficient quantity to accelerate the progress of the reaction, hydrolyzes the fats at the moment of germination?

Might it not be the same in the animal organism? Might not the fats consumed for our alimentation be assimilated in a like manner? We know well the fundamental fact discovered by Claude Bernard in 1849 that the pancreatic juice collected through a fistula emulsifies fats; at the end of a short time the mixture contains free fatty acids. We know also that in 1854 Berthelot showed that the hydrolysis of monobutyrin can be effected by the aid of the pancreatic juice. It seems to be hydrolysis, therefore, which represents the first phase in the assimilation of the fats! We have shown that lipase, a ferment contained in the liver, has an almost negligible hydrolyzing power, although it hydrolyzes ethyl butyrate rather easily; in fact, we were not able to hydrolyze *in vitro* more than 3 per cent. of fat. Our experiments have shown, on the contrary, that steapsin, a ferment contained in the pancreatic juice, has quite a large hydrolyzing power.

Steapsin, without doubt, effects the hydrolysis by emulsifying the fat, finely dividing the fat globules in such a way as to bring them into intimate contact with the water molecules which, in their turn, attack and split up the glycerides into diglycerides, monoglycerides, glycerol, and fatty acids. We thus come back to our fundamental point of view, *viz.*, that it is the water which effects the hydrolysis.

Inasmuch as in the laboratory potash or soda in alcohol (either ethyl or amyl) solution is used to accelerate the process of saponification, it might be thought that alcohol behaves like a catalytic agent. But if the least trace of water is rigorously excluded, the splitting up into glycerol and fatty acids

by means of alcohol is not effected. If sodium ethylate, first recommended by Bouis, freed from all traces of water, is used as the saponifying agent, only the reaction indicated by the equation

$$(2)\quad C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix} + 3C_2H_5ONa = C_3H_5(ONa)_3 + 3C_2H_5OR$$

is realized. Minimal traces of water are sufficient to decompose trisodium glycerate, first into disodium, then into monosodium glycerate, and finally into glycerol and caustic soda. It is the latter which, in its turn, hydrolyzes or, if you wish, saponifies the ethyl esters according to the equation

$$(3)\quad 3C_2H_5OR + 3NaOH = 3C_2H_5OH + 3NaOR.$$

It will be easily understood that in the laboratory operations where caustic potash and soda in alcoholic solution are used, the whole series of reactions enumerated above takes place, ending up in a first phase resulting from the successive reactions, the production of ethyl esters which, in their turn, in a second phase, are split up into glycerol and fatty acids, the latter, finally, being converted immediately into soaps by combining with the potash. If the proportion of potash is less than that theoretically necessary for the formation of soaps, some ethyl esters and a quantity of soap corresponding to the amount of alkali used will be found in the products of the reaction. Numerous experiments have confirmed this theoretical postulate.

The action of alkalies in alcoholic solution must not be considered as differing, theoretically, from hydrolysis in aqueous solution; the alcohol need only be considered as water, HOH, in which one hydrogen is replaced by a C_2H_5 or C_5H_{11} radical. The reaction between the glyceride and alcohol may be represented by the equation

$$(4)\quad C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix} + 3C_2H_5O{-}H = C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix} + 3C_2H_5O{-}R,$$

which sums up the three following equations:

$$(4a)\quad C_3H_5\begin{matrix}\diagup OR\\ —OR\\ \diagdown OR\end{matrix} + C_2H_5O—H = C_3H_5\begin{matrix}\diagup OH\\ —OR\\ \diagdown OR\end{matrix} + C_2H_5O—R;$$

$$(4b)\quad C_3H_5\begin{matrix}\diagup OH\\ —OR\\ \diagdown OR\end{matrix} + C_2H_5O—H = C_3H_5\begin{matrix}\diagup OH\\ —OH\\ \diagdown OR\end{matrix} + C_2H_5O—R;$$

$$(4c)\quad C_3H_5\begin{matrix}\diagup OH\\ —OH\\ \diagdown OR\end{matrix} + C_2H_5O—H = C_3H_5\begin{matrix}\diagup OH\\ —OH\\ \diagdown OH\end{matrix} + C_2H_5O—R.$$

The final products would be glycerol and the ethyl esters of the fatty acids. The possibility of these reactions has not yet been demonstrated experimentally, but with anhydrous products and under high pressures, especially with the aid of a favorable catalytic agent, it is probable that the reaction would proceed largely according to equation (4).

It is thus that we expressed ourselves five years ago, but today our predictions have been confirmed by the alcoholysis effected by Haller. If a fat is heated with 2 parts of methyl, ethyl, or propyl alcohol, containing 1 or 2 per cent. of hydrochloric acid, until a homogeneous mixture is obtained, the neutral glyceric esters are transformed into methyl, ethyl, or propyl esters. Such is the methanolysis, ethanolysis, propanolysis of Haller, a beautiful method which will perhaps aid us in the future in analyzing, qualitatively, at least, the complex mixtures of glycerides contained in a natural oil or fat.

Let us go back and sum up again the mechanism of hydrolysis. It is the water alone which effects hydrolysis, and at a rather high temperature hydrolysis is effected in quite a short time. By adding to the water a catalytic agent, a base or strong acid, the temperature can be lowered and the time reduced. Finally, with a catalytic agent possessing a considerable emulsifying power, such as enzymes, hydrolysis can be effected at the temperature of the blood or even of the soil. This explains how the ferments of seeds or of the pancreatic juice favor the hydrolytic reactions of cellular life.

The same considerations, moreover, permit of a very simple explanation of the rancidity of fats. When rigorously protected from moisture, oils or fats maintain their neutrality

indefinitely. But if they are allowed to stand in contact with the organic matter from which they are extracted, such as the marc of fruits or the animal tissues, the casein of butter, etc., the hydrolysis of the glycerides increases rapidly and may attain considerable proportions. The formation of such a large quantity of fatty acids can be explained as being due to the action of water, favored by the enzymes which exist in considerable quantity and act as accelerators. Admitting that commercial oils and fats contain minimal quantities of ferments, the traces of water which they always retain suffice to effect the initial reaction, hydrolysis.

Such is the primary cause of the formation of fatty acids; such is the prelude, the initial phase, of rancidity. We know that commercial oils and fats contain free acids. Exposed to the action of atmospheric oxygen in the presence of light, the fatty acids undergo a certain modification and the fat acquires a disagreeable odor and a bitter taste. In such a fat the presence of volatile acids and perhaps of aldehydes can be proved; in other words, it has become rancid! We can, moreover, expect to find in rancid oils and fats di- and monoglycerides. Dierucin, which separates in a crystalline mass from rancid oil of colza, confirms in a striking manner this theoretical postulate.

We know that the cell itself effects the inverse reaction, *i. e.*, the synthesis of fats! In animals which consume fats in their alimentation, this synthesis is effected on a vast scale. We might be tempted to attribute this inverse reaction to the action of other enzymes. On the other hand, the opinion has been expressed that all enzyme processes can effect reverse reactions, hydrolysis as well as synthesis. Nevertheless we have not succeeded, in our experiments with steapsin *in vitro*, in producing the inverse reaction, *i. e.*, synthesis. But the number of experiments carried out is still too limited to permit of drawing general conclusions from them. Moreover, Pottevin, having previously shown that mono-olein is obtained synthetically from oleic acid and glycerol under the influence of pancreatic tissues, effected the synthesis of triolein by the action of pancreatic juice on the mono-olein in the presence of oleic acid. This synthesis was, besides, confirmed by Taylor, although this author did not succeed in preparing palmitin and stearin by the same method. But considering the enormous differences which must exist between syntheses *in vitro*, on the one hand, and *in vivo* on the other, these results are not entirely negative. It is nevertheless an

undoubted fact that in the organism there are rhythmical variations leading now to hydrolysis, now to synthesis, according to the local exigencies of the organs.

Let us not think, moreover, that we are already passing beyond the limits of the chemistry of the fats! The practitioner called upon to study the influence which the fat given in alimentation has on the composition of the butter of mammals could suggest no other explanations. We find, moreover, a perfect analogy, purely chemical, in the action of Twitchell's reagent. It was seen above that this reagent accelerates the hydrolysis of fats by water; if it is added to a mixture of fatty acids and glycerides and the water which is formed is eliminated, the fatty acids combine with the glycerol to form mono-, di-, and triglycerides, a reaction which is analogous to the synthesis of the glycerides, first effected by Berthelot. Platinum black can likewise act in a similar manner as an accelerator both of hydrolysis and of synthesis.

Do the synthetic methods for the preparation of the glycerides find an industrial application? The primary substances used in all the methods thus far elaborated being themselves the immediate products which the glycerides yield on hydrolysis, strictly speaking, these methods cannot be regarded as synthetic methods, since the point of departure is, in fact, the product which it is desired to obtain finally! This would no longer be the case if it were possible to prepare the fatty acids synthetically from different primary substances, such as the hydrocarbons found in abundance in natural petroleum. The problem of the synthesis of fats would then be really solved by converting a CH_3 group of the hydrocarbons boiling around 300° into a carboxyl group. Thanks to the method of *Grignard*, it has been possible to synthesize acids containing as high as ten atoms of carbon, and to prepare a di- and a trioctin by heating an octanoic acid with glycerol at 250°.

Will it be possible to prepare a stearin?

It must be remembered that the behavior in chemical reactions of acids high in carbon is essentially different from that of the lower acids.

Decidedly, Nature, silent and indefatigable, works in a manner less rough and, especially, more sure and efficacious than we do!

The biochemical synthesis of the fats is realized, in fact, on a large scale, in nature, by means of water and the simplest compounds of carbon, *viz.*, carbonic acid, aldehyde, etc. What are the consecutive phases which lead thus to the pro-

duction of a fat? As yet we do not know! It seems certain, nevertheless, that vegetable oils and fats originate from the hydrates of carbon.

It was Luca who first showed that mannite is transformed in the fruit of the olive tree into olive oil; Müntz likewise showed that glucose, saccharose, and starch undergo the same transformations in the seeds of the colza, the poppy, and flax.

But such processes do not enter into the domain of industrial application.

Natural oils and fats are, moreover, found in such abundance that their industrial preparation by synthetic methods is of no practical importance. Chemists ought rather to suggest to Dame Nature methods for the amelioration of the quality and for the increase of the quantity of the fats which she produces. Extended investigations must then be undertaken to determine the influence exerted by the seasons, the species of a plant, the climate, the soil, the breed, the nature of the alimentation, and even the idiosyncrasy of an animal, on the quantity and the qualitative composition of the fats. These qualitative variations, however small they may appear, are of the greatest importance for the industry. It is to the influence of the soil that must be attributed the difference in quality of the oils extracted from the Jaffa sesame, on the one hand, and from the Chinese sesame on the other. The same is true for olive oil from different sources! The investigations on oils now being carried out in Algeria and Tunis demonstrate strikingly the necessity of combining purely chemical researches with physiological, agronomic, and economic investigations in order to secure to the industry of the fats the coöperation of science.

As soon as the importance of the soil was recognized, the study of the proper methods to effect the amelioration of seed and fruit species, as the stock breeder has been doing for centuries, was begun. In the United States it was attempted to produce two varieties of maize seed, one containing a large proportion of oil, the other a small proportion. Here are some figures: Within the course of seven years it has been possible to produce a variety whose content of oil increased from 4.7 per cent. to 6.53 per cent.; inversely, another variety has been obtained whose content of oil has fallen from 4.7 to 2.97 per cent. By transplanting flax seeds rich in oil in soils where only seeds poor in oil are obtained, a decrease of the oil content is observed. American and Egyptian cotton seeds con-

tain about 23 per cent. of oil; when transplanted and cultivated in Bokhara they contain only 17.5 per cent.

What is the cause of this decrease? We do not know! It remains then for science to study these phenomena, still obscure at the present day, to choose and cultivate the species rich in oil; the farmer shall utilize these investigations and derive from them practical principles!

Meanwhile, the oil manufacturer is compelled to make these selections himself.

In fact, in order to manufacture edible oils, he selects the freshest and soundest fruits and seeds. Expressed cold, they give him almost immediately oils fit for consumption. Thus, for example, Jaffa sesames and Rufisque peanuts are the most highly esteemed for the production of table or margarin oils, while seeds from other sources furnish hardly any but ordinary edible oils or even oils for industrial purposes.

Thanks to its geographical situation and to its climate, France, and especially Marseilles, have played a most important rôle in the industry of oleaginous substances. It will be well then to sketch the history of its development in a brief historical review of the French and Marseilles oil industry.

The cultivation of the olive tree, introduced into France by the Phoenicians, gave birth to the industry of olive oil. It was formerly an agricultural industry, the precursor of the oil industry of our times. The fruits were triturated in a mill and the marc expressed by means of a screw press, analogous to the presses employed for grapes. The hydraulic press, conceived by Bramah in 1795, introduced a new source of force, easy to direct and of almost unlimited power. Bramah's invention brought about a complete revolution in the oil industry and it was not long before it attracted the attention of the Marseilles manufacturer. New seeds were introduced, the Marseilles press became widely distributed and its utilization was increased by the use of scourtins; the accumulator invented by Armstrong in 1843 was adopted. Thanks to the introduction of steel, a substance having an enormous resistance, the pressure, formerly limited by the resistance of the screw to rupture, was raised to 250–300 atmospheres. The press manufacturer's material permits of surpassing these pressures, but the use of the scourtins, of which the Marseilles people are so fond, prohibits it.

It was, moreover, not in one day that this degree of perfection was attained.

The first attempts to triturate flax seeds from the Levant date back to 1817. The same materials and the same method were used as in the manufacture of olive oil.

The north of France was competed against. There the wooden screw press was employed to express the seeds (native-grown) of the hemp, the mustard, the garden-poppy, the colza, and the flax; then it was replaced by the lever press and, shortly afterwards, by the wedge and cam press which had been used by the Chinese for centuries (and invented again in Holland in the 17th century). The cultivation of the colza, moreover, began to give way to that of the beet; the cultivation of the garden-poppy likewise decreased. The North had no more seeds to pour out upon Marseilles factories, the drain upon which increased with the daily augmenting population.

Marseilles, "the outlet of France on the Mediterranean," then turned towards the sea. The north of Africa possesses olive oil in abundance and it was already being exported as early as the 10th century. But this oil was generally prepared in the same manner in which the Dahomey negro prepares palm oil to-day, *i. e.*, by placing the fruits in a hole dug in the ground and waiting till fermentation of the mass makes the oil rise to the surface. African olive oil thus obtained, sharp, bitter, nauseating, could not suit the fine taste of the Frenchman, accustomed to the virgin oil of Provence. The oil industry did not yet exist south of the Mediterranean; there were not yet exported those large quantities of olive oils which are now brought to Marseilles for use in cutting the native oils.

The countries to the right and to the left of the Cannebière were then turned to and the sesames and poppies of Levant, the peanuts in the shell of the Cape Verde Islands and of Senegal were found. The oils of the first expression were easily sold as edible oils; the oils of the second and third expression found an outlet in the industries. The cake was given to cattle or returned to the soil as fertilizer for the early crops.

The native of Marseilles says that the Cannebière extends as far as India. It is not astonishing, therefore, that the sesames and poppies of India, the peanuts of Coromandel, the copras of Ceylon, and the mowrahs of India were brought to him. From the African coast arrived the palm oils and nuts! Finally there were imported seeds, the oils from which are

suitable only for the industries, the cottons of Egypt, the flaxes of Russia, and the colza of India.

The manufacture of seed oils became the monopoly of the large establishments of Marseilles and this city, with its 49 oileries and 1,557 presses, employing 3,726 laborers, working up daily 1,200 to 1,300 tons of seeds, reached its zenith in 1878. The oil industry extended as far as Bordeaux.

And the North, what was it doing while these rapid advances of the South succeeded each other? We have already mentioned that the colzas had given away to the beet. The oil of colza, for purposes of alimentation, had, moreover, been gradually rejected as the taste of the consumer grew more refined. The cultivation of the garden-poppy was of too small importance to be able to replace it. Alimentation requires solid fats, cow butter, lard, beef and even mutton tallow. But butter was a luxury for the purse of the workingman, and lard itself was dear, for at that time those immense importations from the United States of lard and its substitutes, artificial lards, mixtures of beef and cotton fats, containing but little or even no pork fat, were not yet known.

At this point the government stimulated inventive genius and started up a competition for the industrial production of a fat suitable for consumption, keeping well, and cheaper than cow butter. Mège-Mouriès put his process into practice in 1870 and the margarin industry became established in Paris, where it disposed of considerable quantities of beef tallows, furnished, with all the necessary properties and freshness, by the slaughter-houses of the metropolis. This new industry had first to overcome the popular prejudices which opposed its legitimate development. Neither the calumnies of detractors nor the machinations of the agrarians were able to prevent it from extending, almost triumphantly, into all the countries of the world, even into Australia, a country which is, *par excellence*, a producer of cow butter. Was it not, moreover, a real advantage to the working population, in the sense that it did away with the consumption of unwholesome fats from diseased animals and fats prepared under conditions of doubtful cleanliness? The progress of this industry could not be demonstrated more eloquently than by giving the statistics of production (Table VII):

Table VII.—Production, Imports and Exports of Margarin, in Kilograms.

County.	Estimated production.	Imports, 1906.	Exports, 1906.
Holland	75,000,000	56,210,100	53,890,800
Great Britain	50,000,000	55,479,100	805,700
United States	50,000,000	.....	.....
Germany	25,000,000	168,600	108,700
Denmark	26,000,000	8,710,000	360,000
France	25,000,000	65,663	6,366,930
Sweden	15,000,000	519,600	655,600
Norway	15,000,000	29,400	755,400
Austria-Hungary	15,000,000	792,400	1,406,200
Belgium	11,000,000	359	250,297
	307,000,000		

We may add that in the same year the exports of French butter, fresh and salted, amounted to 19,760,000 kilograms, the imports being only 5,172,000 kilograms.

By establishing the industry of edible animal fats, the North began to dispute the leadership of the South in the field of the fats. Marseilles, thus threatened, redoubled her efforts! She too must manufacture solid fats for consumption. But she turned to vegetable fats! The freshest copras were subjected to treatment, processes of refining were invented, and by going back to the known methods of Braconnot, Chevreul and Dubrunfaut the oil was freed from its original odor and taste. Vegetable butters appeared on the market! In imitation of the processes of the stearin and margarin industries, the liquid parts, the olein, were extracted by pressure from the solid oils, and the quite modern manufacture of substitutes for cacao butter, known as "chocolate fats," was established.

During the course of this contest for the supremacy in the fat industry, the power of the Marseilles press began to be doubted. In foreign countries the fat industry had acquired gigantic dimensions, especially in England, the United States, and also Germany. There had been installed the so-called Anglo-American presses, then the powerful cage presses of the most modern construction. These presses also made their appearance in Marseilles, but whether the patriotism or traditionalism of Marseilles was too strong, or the slow but sure operation of the Marseilles press really was superior, no

great enthusiasm was ever manifested at Marseilles for this modern machinery.

Let us not forget, moreover, that the Chinese, with a primitive wedge press, by prolonging the pressure a whole night obtain a better yield than is secured with the most modern European presses.

Will these efforts to perfect her machinery, improve and develop her manufacture of edible oils, and create new, solid, alimentary fats, bring Marseilles to a new zenith greater than the first? In any case, at the present time Marseilles works up more than half of the oleaginous imports of France, greatly outdistancing her rivals, Bordeaux, Dunkirk, Havre, Dieppe, and Nantes.

Moreover, Marseilles does not limit herself to the expression of oleaginous fruits and seeds. Black olives, which cannot be used for feeding stock, contain too much oil to be rejected. So Marseilles has long since extracted them with carbon bisulphide, a method brought from England by Deiss and still utilized at present in the South. This process is extended to the treatment of damaged castor beans and sesame seeds and the nonalimentary oil cakes. Petroleum ether, employed on a large scale abroad, in England, Germany, and America, has not secured a foothold in the South; but it is not always on account of her conservatism, which, moreover, is legendary, that Marseilles opposes innovations! Quite recently, in fact, extraction by means of carbon tetrachloride, extolled as the ideal of all solvents on account of its noninflammability, has been tried industrially. But the practical manufacturer soon found that the advantages so much preached were rather illusory than real. The cost of the solvent is too high, and the machinery, whose resistance to the attack of the hydrochloric acid liberated by the solvent in the presence of traces of moisture is more than doubtful, is itself too expensive, and so the use of carbon tetrachloride has already been abandoned.

France imports, on an average, 800,000 tons of oleaginous substances, valued at about 270,000,000 francs, and exports about 50,000 tons, valued at 38,000,000 francs. Deducting the fruits of the olive tree, French soil produces less than a tenth of this amount. The production of oil from native fruits and seeds, including olive oil, amounts to about 150,000 tons, of which 15,000 to 16,000 tons are olive oil. France imports 115,000 tons of different oils and fats and exports

50,000 tons, so that the consumption amounts to about 120,000 tons.

The English industry of oleaginous products, nevertheless, surpasses by far that of France. Germany already imports nearly 1,000,000 tons of oleaginous substances, but exports about 300,000 tons. Nevertheless, the native production of flax and colza is not negligible.

Why is Marseilles, formerly the great metropolis of fats, losing its monopoly? Why do those ships laden with cotton from Egypt and Bombay, colza from India, sesame from the Levant, India, and China, palm nuts from Africa, pass by Marseilles and Bordeaux, carrying with the oleaginous products the real industries of Marseilles?

Those are questions which touch upon political economy. It is not for us to discuss them, therefore, especially at this time when it is proposed to place an import tax on oleaginous products.

Moreover, it should be pointed out that the cultivation of oleaginous seeds is decreasing in Europe and that the cultivation of wheat and the beet is more and more gaining the ascendancy. Except in the cultivation of the olive tree, which requires the warm climate of southern Europe, Russia alone still plays in Europe an important rôle as a producer of oleaginous products.

The United States and South America have become formidable competitors of the flax and cotton seed producers of the old world, but it is especially as purveyor of maize and animal oils and fats for the old world that the new world means to establish itself! Brazil itself is ready to put on the market its considerable wealth of solid vegetable fats.

Does the old world therefore run the risk of being suppressed? We do not think so. The production of oleaginous substances in the warm countries—tropical and western Africa, India, Indo-China—can be indefinitely increased. The colonial exposition of Marseilles gave us a vivid illustration of the sources of oleaginous products which are awaiting exploitation through the development of the means of communication by land and sea. China herself seems to be awakening from her slumber; she exports peanuts, sesames, vegetable tallow, in quantities which yearly increase. At this very moment she is sending us Soja beans, the oil from which bids fair to become a competitor of cotton and maize oil.

Such are the raw materials in the industry of the fats! A considerable quantity, which moreover is increasing from

day to day, finds use in the industry of edible oils and fats, but the greater part is employed in the great industry of the fats, the stearin and soap trades.

The processes of the stearin industry are well known; the candles exhibited in successive expositions by French houses have shown to the whole world the importance and the degree of perfection attained by this industry, one of the monuments of French chemical industry. Gas and electricity keenly compete with it, but the production does not suffer much therefrom. For gas are required a large establishment, long piping, cocks, matches. For electricity boilers, motors, electric wires, special lamps, are necessary. And then the consumer is not protected from a possible strike. As to the candle, it is carried in the pocket. The candle and a match, there is the whole installation. It is the ever-ready light! It ought to have been invented if it had not already existed.

The stearin industry no longer witnesses those great inventions, the admirable succession of which marked an epoch in its history; the great efforts of the first half of the last century seem to have exhausted its sources. It is only these details, those difficulties in the recovery of materials, those little economies of raw substance and labor which make the success of a factory and make the greatest demand, perhaps on the perseverance and ingenuity of the practitioner. New materials are therefore sought, palm oils, mowrahs, Illipés, vegetable tallows, bone tallows, regenerated fats, etc. The advantages offered individually by saponification with lime under pressure, on the one hand, and with sulphuric acid on the other, the one giving a greater yield of glycerol of better quality, the other a greater quantity of solid acids, are combined. It is the "mixed process" of the modern stearin industry. Saponification by means of Twitchell's reagent, representing another kind of "mixed process," has already been mentioned above. The fats are hydrolyzed with this reagent, the product of hydrolysis acidified with concentrated sulphuric acid, in order to transform the oleic acid into solid products, and the mass distilled in the usual way. The presence of a considerable quantity of free fatty acids being one of the essential conditions in this process it is especially adapted to the utilization of inferior fats. The large slaughter houses of Chicago supply considerable quantities of these. This is why this process has extended to several establishments in the United States. Nevertheless, a number of disadvantages are attached to it, and it has not been able to pene-

trate into and maintain itself in any European stearin factory.

Another innovation! In the attempt to do away with the pressing out (hot or in the cold) of the fatty acids, it was discovered that a dilute solution of sulphostearic acid dissolves oleic acid alone, the solid fatty acids remaining undissolved in this medium. We have seen this process applied industrially in the factory of the inventor at Turin.

A new rival of stearic acid appears in mineral waxes. The French stearin industry, always proud of its reputation, has thus far refused to use those American and Scotch paraffines which are used abroad in enormous quantities. The French consumer demands a beautiful, hard, brittle candle of high melting point. But now that paraffines from Rangoon and Assam are obtained which melt higher than stearin itself, it will not be long before the lure of low cost will attract to them the attention of the French stearin manufacturer.

A great problem of the stearin industry still remained to be solved, *viz.*, the complete transformation of oleic acid into stearic acid. Just like stearic acid, oleic acid contains 18 atoms of carbon and 2 atoms of oxygen, but differs from it by having two atoms of hydrogen less. One of the easiest processes in the domain of organic chemistry to carry out is hydrogenation by means of sodium amalgam. Nothing simpler than to treat the oleic acid with this reducing agent in order to convert it into stearic acid, a substance which is ideal for the stearin industry! But oleic acid rebelliously refuses to take up hydrogen under these conditions. The same is true of its mono- and dibrom derivatives, an indirect method which it seemed to us useful to try.

Saponification with sulphuric acid pointed out the way which it seemed should lead to the conversion of oleic acid into solid substances, and for the last fifty years this reaction has been thoroughly studied. But reversible reactions intervene, and large quantities of oily products which cannot be utilized are formed.

It was attempted to prepare palmitic acid, a substance well adapted to the needs of the stearin manufacturer, by fusing oleic acid with caustic alkalies, and Olivier and Radison installed such a plant in the stearin factory of Fournier, at Marseilles; but the candles so obtained, which were exhibited at the exposition in 1878, have a rancid odor and feel greasy, and this process has been abandoned.

Hydrogenation by means of electric discharges in an atmosphere of hydrogen was then thought of.

With the classic work of Sabatier and Senderens as guiding thought, it was later proposed to use metallic cathodes of palladium, platinum, and nickel, covered with a spongy layer of the same metals, in an alcoholic solution of oleic acid. But it is not such methods which will lead to the goal! It is rather the method of Sabatier and Senderens which marks a new era in the history of the solution of this problem.

Very shortly after the publication of the first monumental researches of these scientists on the hydrogenation of organic bodies in the presence of finely divided nickel, a German plant took out a patent for the conversion of unsaturated fatty acids or their glycerides into solid substances. Having already carried out laboratory experiments based on the principle of the method of Sabatier and Senderens, we repeated the experiments described in the patent, but were unable to obtain marked reduction. The product cakes together and contains nickel oleate. As far as we are aware, moreover, this process has never entered into the domain of practical industry.

Taking up again our study of the reaction of Sabatier and Senderens, we succeeded in obtaining a quantitative yield of stearic acid. Our first lack of success was probably due, then, to the fact that our contact substance had become inactive. We would say in the modern language of chemistry that the nickel was "poisoned." Almost simultaneously, Bedford and Williams took out a patent for the reduction of organic substances by the Sabatier-Senderens method; Schwoerer likewise had patented an apparatus for the transformation of oleic into stearic acid by the contact process. Finally, Sabatier himself has taken out a patent on this subject.

But this is not yet the final word. Paal and Roth recommend a hydrosol of palladium as a catalytic agent and carry out the hydrogenation at ordinary temperature. Olive, castor, and cod liver oils are converted almost completely into solid saturated fats. Oleic acid is thus reduced, in large part, to stearic acid. Here is enough, then, for the near future for the stearin manufacturer.

No one is ignorant of the considerable development which the soap industry has undergone during the last few years, and it is known that there are immense establishments where household soap is produced daily by the hundreds of tons.

It is not "augmented" or "charged" soaps which are manufactured and sold in such large quantities. They are soaps of

a degree of purity such as the imagination of the soapmaker of the first half of the last century could not have conceived, soaps free from caustic alkali and practically free from carbonate of soda. They are soaps containing from 63 to 64 per cent. of fatty acids—the maximum amount which a boiled soap can contain—and 29 to 30 per cent. of water.

In a word, it is the purity of household soap which characterizes the soap industry of to-day. The consumer becomes more and more exacting, demands not only a pure soap, but one of a firm consistency, not too hard, and of an agreeable color. The thrifty housewife who used to lay away her soap to dry above the stove or hearth to remove the excess of water has well-nigh disappeared. Time is money! Those excessively hard soaps made of olive oil or beef tallow, sole assets of the soapmaker of bygone days, are no longer wanted!

The mottled soap of Marseilles, that soap of legendary repute, contains only 58 to 59 per cent. of fatty acids; its water content is as high as 35 per cent.; moreover, it contains a few per cent. of mineral salts. It is therefore no longer a pure soap according to the definition given above. That is why its consumption and manufacture, formerly considerable, are gradually decreasing, even in the South, its native soil.

The mottled soap of Marseilles, the product of the slow evolution of that happy symbiosis of olive oil and saliferous plants, suffered its first serious modification as a consequence of the brilliant discovery of Leblanc. The soap resulting from boiling olive oil with the lyes obtained with artificial soda was harder than its predecessor, and the olive oil was mixed with walnut and poppy oils. Curious thing, such an addition was then considered as fraudulent! But the ordinary oils of sesame, peanuts, palm nuts, and cocoanuts, which needed an outlet, forced themselves in increasing quantity on the attention of the soapmaker. They began to be employed and even to be substituted completely for olive oil, and it is thus that the manufacture of pure, uniformly colored soap, which will before long give the death blow to mottled soap, arose.

The intelligence of the soapmaker is manifested in his skill in mixing the raw materials placed at his disposal in such a way as to obtain a soap exactly adapted to the desired purpose. In that consists the art of the soapmaker of our day.

That is why, while still using the open pan method of work, he studies experimentally the individual properties of the raw materials in order to derive from them practical formulas. In this connection we recall with satisfaction the work of

Merklen. Let us hope that it will stimulate the scientific activity of the French soap factories!

The saponification of neutral fats in the open pan is the natural process of the soapmaker. It is the one which gives us products of the best quality, beautiful color and suitable hardness. It gives us at the same time saponification lyes which contain almost all of the glycerol of the neutral fats, the extraction of which offers no difficulty, providing the alkaline lyes used are pure, a condition easily obtained at the present time. The modern soapmaker no longer pours his exhausted lyes into the river or sea, he keeps them and treats them scientifically to recover the "crude glycerol of the lyes," which, thanks to the invention of Sobrero, pupil of Pelouze, is so easily disposed of in the markets of the world.

The profits which the recovery of the glycerol brought to the large soap factories of France, England and the United States soon attracted the attention of the countries where the manufacture of soaps was still in that intermediate state of evolution of an industry trying to rise from the condition of a small trade, *quasi* domestic, to that of a great chemical industry. New methods were sought and, going back to the known processes, the manufacture of soaps from oleic acid, a sister industry to the stearic industry, was imitated. It was attempted to introduce into the soap factories the autoclave, thanks to which would be obtained the glycerol from the saponification, and fatty acids yielding soaps by simply neutralizing with carbonate of soda! The small soapmaker, mistrusting claims as persistent as they were insistent, at first refused to adopt machinery of which he knew only the dangers of explosion. That is why we saw arising those "deglycerinating" establishments where the glycerol is extracted by means of the autoclave. The fatty material was offered to the small soapmaker as raw material, as an inducement for the adoption of a process which was more economical and gave a better yield. But the soap is of an inferior color and consistency! It was attempted to remedy these serious defects and the pressure in the autoclave was diminished to five or six atmospheres and zinc oxide and powder were used. In this way the hydrolysis is reduced to about 80 per cent. and the yield of glycerol is decreased, while it is impossible to obtain a soap which can compete in quality with the product of the open pan process. Moreover, the costs of manufacture are not lower than with the latter process.

Decidedly, it was not the ideal process for the manufacture

of soap! Truly, soap could not be lowered to the level of a by-product, and in the end the great soap factories of the world did not adopt this method. We have even seen in several soap factories the machinery for heating in the autoclave idle, industrial experience having shown that the principal product, soap, was of a quality distinctly inferior.

Before long there appeared two rival methods for deglycerinating fats, both of which furnished a crude product still containing 15–20 per cent. of neutral glycerides. Great claims were also made for them, a thing which truly seems inseparable from everything connected with the soap industry! These were fermentative hydrolysis and the Twitchell process, the latter originating from the stearin industry and adapted to the exigencies of soap manufacture.

The criticism made above is also applicable to these two processes. Although yielding a product of better color than the autoclave process, fermentative hydrolysis involves considerable losses of fat; moreover, the raw material to be hydrolyzed must not melt higher than 35° nor contain any considerable quantity of free fatty acids. The Twitchell process, on the other hand, is better adapted to raw materials rich in free fatty acids. It is the process to be preferred for short tallows, waste fats; but it goes without saying that soaps made thus are also darker.

But the pursuit of glycerol did not yet stop here. Going back to the beginning of the stearin industry, the saponification with lime in open vessels was revived with this modification (which, to be sure, is useful) that the heating was not continued till the lime soap became hard and brittle. Some small soapmakers adopted this process especially for nauseous bone fats, which the lime deodorizes, while, at the same time, saponifying them. But the glycerol obtained is easily susceptible to fermentation, the operations are long, wearisome, the losses considerable, absorbing the profits which the recovery of the glycerol would bring.

We do not believe that there is any future for the deglycerinating processes. It is still the open pan process which will carry off the palm to-morrow, as it has done yesterday. Let the price of glycerol go down and these processes, whose existence is already ephemeral, will cease to be applied!

But happily for the soap industry, the lowering of the price of glycerol is still far off. That is why the small factories themselves are hastening to adopt the most perfect machinery

for the evaporation of the liquors of the soap industry, *i. e.*, for the evaporation in a vacuum.

The crude glycerol of the lyes of the soap factories is to-day obtained in such a state of purity that the greater portion of dynamite glycerols are obtained from this source. Nineteen years ago we prepared, on a large scale, the first chemically pure glycerol by starting from the crude glycerol of the lyes. Since then many establishments prepare chemically pure glycerol in the same way.

The quantities of glycerol extracted from the lyes of soap factories are rapidly increasing. A personal estimation leads me to evaluate the production of glycerols in France at 15,000 to 16,000 tons a year, *i. e.*, 7,500 to 8,000 tons of saponification glycerols of 28° Bé. (of which 2,000 tons are obtained from soap factories which use the deglycerination process, and 4,5000 to 5,000 tons from the stearin industry), and 7,500 to 8,000 tons of crude glycerols from the lyes of soap factories. We estimate that Great Britain produces about 25,000 tons a year and the United States 13,000 tons. For the other countries we have been unable to obtain authentic data.

A by-product which yesterday was cumbersome, even embarrassing, glycerol is to-day the plank which saves the soap factories. It is the recovery of the glycerol which binds the soap industry to the great chemical industries of modern explosives!

The industry of the fats is based on solid foundations. Nature gives us the raw materials in unlimited, inexhaustible quantities; science teaches us the methods for transforming them into useful derivatives of greater value; the manufacturer applies these methods to the raw materials to increase the well-being and the comfort of the human race.

Now, as in the past, the stearin and soap industries hold an honorable rank in the hierarchy of industrial chemistry! And yet these industries seem to us but to barely touch on the confines of the industrial domain of the fats. It is but the first stage in the victorious march of the industry of the fats! The chemistry and industry of boiled oils, the chemistry and industry of oxidized and ozonized oils, of vulcanized, iodated, brominated, chlorinated, sulphonated, nitrated oils, the industry of soaps with metallic bases, and a multitude of others, but await the coming of ingenious inventors.

And just as the first application of chemical analysis to the fats led, with so much success, to the creation of the stearin

industry, likewise the future progress of the industries of fatty substances will depend on the development of the chemical analysis of fats.

Lost in the darkness of the development of the soap industry, analysis first appears in the 18th century. Geoffroy, Junior, and Maquer published some analyses of soap. They determined the quantity of water by evaporation; they separated the fatty substance, still considered as the original fat, by means of hydrochloric acid and weighed it. These are the methods still employed to-day to determine the content of water and insoluble fatty acids. They determined also the quantity of alkali, weighed as sodium chloride or carbonate. Chevreul, employing analysis with an extraordinary skill and ingenuity, discovered stearic, margaric, oleic, and the volatile butyric, caproic and capric acids; he gave also very clear indications as to the existence of a phocenic and a hircic acid. The method of separating the volatile and insoluble fatty acids, a problem which even at the present is not yet solved in a perfectly satisfactory manner, was thus brought out. Then Chevreul attacked the problem of the separation of oleic from the saturated acids and solved it in a way which is truly surprising.

Three great groups of fatty acids—volatile, insoluble, unsaturated—were clearly distinguished, were established. It remained to fill some gaps. Boudet, while studying Poutet's reaction, found elaidic acid; Fremy isolated palmitic acid (a discovery which is important in the sense that it contributed to elucidating the nature of margaric acid); Bussy and Lecanu added a new class of fatty acids, that of ricinoleic acid. The work of the French school drew attention abroad; myristic, lauric, behenic, archidic, erucic, hypogeic acids were isolated.

But these were only the first foundations, however solid they might be, laid down whereon to build the edifice of the analysis of the fats. The practitioner, forced to get his bearings in the midst of the disconcerting multiplicity of the fats, had need of clear, even rapid, methods for discovering the adulterations which unscrupulous manufacturers and merchants imposed on commerce with that impunity which borrows its strength from the powerlessness of the chemist. He then had recourse to the determination of the specific gravity, of the melting and freezing points, and of a few other physical properties, to the test for elaidin, and especially to those

color reactions which still have too much attraction for a number of chemists, especially in France.

It was not yet clearly seen, as we showed 15 years ago, that all color reactions are due to foreign, adventitious substances, dissolved in the oils and fats. Most of these substances, supposed to be characteristic, have now disappeared from the commercial products, and there remain but the reaction of Baudoin for sesame oil and that of Halphen for cotton oil. Even these, considered thus far as precious reactions in qualitative analysis, are beginning to lose some of their importance.

It was especially owing to the lack of better methods that these color reactions flourished. Quantitative methods were needed!

Cailletet first proposed, in 1857, to determine the quantity of bromine absorbed by various oils and fats. It is the prototype of that modern method of the iodine number, a method of the most precious generality and reach for the identification of oils and fats, indicating in a certain manner the class or group to which belongs each natural oil and fat. The elaboration of the quantitative methods pointed out by Chevreul was continued. Oleic was separated from palmitic and stearic acids, the soluble from the insoluble acids.

Going back to the method applied by Chevreul, the quantity of alcoholic potash necessary to effect the complete saponification of each oil and fat was determined, and this determination was made by the volumetric method recommended by Gay-Lussac.

There were then found those important numbers which make it possible to differentiate in a manner as rapid as it is exact cow butter and cocoa oil on the one hand and colza oils on the other from most of the ordinary oils and fats. The iodine number, the saponification number and Reichert's number became the ordinary tools of the expert chemist charged to discover the adulterations of foodstuffs.

It was especially the adulteration of edible fats and oils, of butter, lard, olive oil, which had constrained the public analyst to elaborate these so-called quantitative methods. And the analyst was master, even if but temporarily.

Adulterations becoming more complex and more and more subtle, new methods, of a greater degree of perfection, to conquer the adulterator, had to be devised. Thorough study of the work of Chevreul led to methods based on the difference of solubility; Maumené studied and applied the thermic test

with sulphuric acid; Amagat and Jean introduced the oleo-refractometer.

But the adulterator kept pace with the progress of analysis and he soon adapted himself, with an extraordinary skill, alas, to the methods employed by the public analyst. With an ingenuity worthy of a better cause, the adulterator takes advantage of all those variations and anomalies which Nature presents in the oils and fats which she furnishes us.

It was therefore necessary to start again, and again the work of Chevreul was gone back to!

But do the known fatty acids exhaust all the possibilities, all the variations of which Nature may be capable? No! A thorough study of the drying oils showed the existence of linolenic and of linoleic acids, representatives of two new series of fatty acids; Arnaud's tariric acid is related to linoleic acid. Juillard found a dihydroxyl acid in castor oil, and even natural bibasic acids were discovered. But it is not only open-chain fatty acids which Nature uses for the synthesis of fats! For now there were discovered cyclic acids having rotatory power, the chaulmo-ogric and hydnocarpic acids extracted from chaulmo-ogra fats and their congeners by the happy hand of Power.

Stearic acid, a saturated acid with 18 carbon atoms, contains 36 hydrogen atoms; oleic acid contains two atoms less, and it absorbs two atoms of bromine or iodine.

Linoleic acid contains four atoms of hydrogen less and absorbs four atoms of bromine or iodine. Chaulmo-ogric acid, isomeric with linoleic acid, absorbs only two atoms of iodine, but as we have already pointed out, it contains a cyclic grouping. Linolenic acid contains six atoms of hydrogen less than stearic acid and absorbs six atoms of bromine or iodine. All these unsaturated acids can be converted into stearic acid by the method of Sabatier and Senderens.

Is linolenic acid the least saturated of the natural acids containing 18 atoms of carbon which are found in natural fats? Fish oils absorbing about the same quantity of iodine as the drying oils often attracted the attention of analysts. But it is only quite recently that a thorough examination disclosed in the oils of marine animals the existence of a new acid in considerable quantity. It is clupanonoic acid, containing 18 atoms of carbon and 28 atoms of hydrogen; it absorbs eight atoms of bromine or iodine. There is no doubt

that this acid can be transformed into stearic acid by suitable treatment.

On the other hand, a thorough study was begun of those foreign substances, the oils and fats comprised under the name of unsaponifiable substances. Among them was discovered cholesterin, an important member of the group of adipoceres, already studied by Chevreul. The great master had already recognized its alcoholic nature. Phytosterin, "the cholesterin of plants," was also found.

The investigations of Bömer, as painstaking as they were important, showed clearly that all oils and fats of vegetable origin are characterized by the presence of phytosterin (now called sitosterin), and all oils and fats of animal origin by the presence of cholesterin.

Here is a difference of great importance! It is chemical analysis apparently introducing us into the mysteries of the laboratory of Nature, disclosing the system by which she works. The tests for the acetate of phytosteryl, based on these investigations, gives us a means of classifying oils and fats according to their origin as vegetable or animal oils. That is not all! It allows us to discover minimal quantities of vegetable oils and fats added fraudulently to oils and fats of animal origin. Minimal quantities of cocoa oil in cow butter, or a few per cent. of cotton oil in lard, can be disclosed with absolute clearness.

Yet a little while and we shall be able to solve the inverse problem, the detection of small quantities of animal oils and fats in vegetable oils and fats. Olive oil will then no longer be adulterated with lard oil!

The test for the acetate of phytosteryl and the iodine number are, in a word, the two great principles, based on analysis, which we have adopted to establish a classification of the natural glycerides. We propose a natural division into fats of vegetable and of animal origin, and a subdivision into liquid fats, or oils, and solid fats of vegetable and animal origin. *Natura non facit saltum*; so too, we cannot expect a very sharp division.

The main features of analysis sketched in our rapid review lead then to more detailed subdivisions.

Here are these divisions brought together into a synoptic table:

Table IX.—Fats.

I. Oils and Fats of Vegetable Origin.

A. Vegetable oils.

1. Drying oils.
2. Semidrying oils.
   - *a*. Cotton oil group.
   - *b*. Colza oil group.
3. Nondrying oils.
   - *a*. Almond oil group.
   - *b*. Olive oil group.
   - *c*. Castor oil group.

B. Vegetable fats.

1. Chaulmo-ogra oil group.
2. Laurel oil group.
3. Palm oil group.
4. Nutmeg butter group.
5. Cacao butter group.
6. Cocoa oil group.
7. Dika butter group.

II. Oils and Fats of Animal Origin.

A. Animal oils.

1. Oils of marine animals.
   - *a*. Fish oils.
   - *b*. Liver oil.
   - *c*. Blubber oils.
2. Oils of land animals.
   - *a*. Semidrying oils.
   - *b*. Nondrying oils.

B. Animal fats.

1. Drying fats.
2. Semidrying fats.
3. Nondrying fats.
   - *a*. Body fats.
   - *b*. Milk fats.

Drying oils of vegetable origin are characterized by their content of linolenic acid; semidrying oils by the presence of linoleic acid. The two groups of cotton and colza oils are differentiated by their saponification numbers, the presence of erucic acid in colza oils producing a considerable lowering of this number.

The class of nondrying oils, with the exception of the castor oil group, which contains considerable quantities of ricinoleic and other hydroxylated acids, is characterized by the preponderance of oleic acid. The almond oil group still contains small quantities of linoleic acid. Peanut oil, which belongs in the olive oil group, contains arachidic acid, which is determined by Renard's method.

Among the vegetable oils, the polarimeter distinguishes the chaulmo-ogra group.

The members of the laurel oil group still contain considerable quantities of oleic acid.

With palmitic acid predominating, we come to the palm oil group; with myristic acid, we have the nutmeg butter group. When the proportion of oleic acid decreases considerably and that of stearic acid begins to become more pro-

nounced, we reach the representatives of the cacao butter group.

Oils containing volatile acids in considerable quantity constitute the group of cocoa oil. The same oils are characterized by considerable quantities of lauric acid. When the volatile acids disappear while lauric acid still preponderates, we reach the dika butter group.

Let us consider in the same way the oils and fats of animal origin. The oils of marine animals are characterized by clupanonoic acid, those of land animals by oleic acid. The drying and semidrying fats of animal origin contain acids less saturated than oleic acid, perhaps isomers of linolenic and linoleic acids, if not clupanonoic acid itself, which seems probable, at least for the fat of the polar bear.

The nondrying animal fats are divided into two groups, the body fats and the milk fats, both being clearly differentiated by the absence or presence of volatile acids. Milk fats are the perfect analogues of the cocoa oils!

By adopting this point of view, the table above shows us what path analysis must in the future follow, combining its methods with purely scientific investigations in order to make new conquests. This alliance, while helping industry, will also furnish the public analyst, who is all at sea and is already appealing to the law for aid, with the indispensable weapons for the bitter and ever renewed warfare which he is waging with adulterators.

For a time it seemed that analysis did not find support in the fertile soil of Chevreul's native country. But for some time now efforts in this direction have been redoubled. Müntz and Coudon are showing the analyst how to detect small quantities of cocoa oil in cow butter; Haller is beginning to penetrate more deeply into the composition of natural fats; others follow him.

The ideal of a complete analysis of the fats is to effect the isolation and identification of all the acids of which it is composed, just as the elements of a mineral are isolated and identified. A task which cannot be realized to-day; it will be the problem of to-morrow!

It is almost a century since Chevreul made that memorable analysis of a soap which laid the foundations on which has arisen the modern edifice of the fats through which we have just passed. May another Chevreul rise in this midst, where the genius of the master has not ceased to inspire brilliant successors.

Let us cultivate analysis! It will fructify the chemistry as well as the industry of the fats! J. LEWKOWITSCH.

THE PREPARATION OF ALCOHOL AND ARTIFICIAL SILK FROM CELLULOSE.

Several recent articles, one on the preparation of alcohol[1] from sawdust and other wood waste, and the others on the preparation of artificial silk[2] from cellulose, both in the form of cotton and wood, are of special interest at this time when the question of the conservation of the natural resources and the utilization of waste materials is regarded as of fundamental importance for the present and future welfare of the race. Any method which will enable us to make use of waste products will be of great value, and although at the present time much of the artificial silk is made from cotton, waste cellulose materials are being used, to some extent, in its production, as in that of alcohol. Practically all of the commercial alcohol is prepared by the fermentation of sugars obtained by the hydrolysis of starch or from fruits or the noncrystallizable by-products of sugar works. At the present price of corn, about $25.00 per ton, as one ton of corn produces about 90 gallons of 94 per cent. alcohol, the cost is about 28 cents per gallon for raw material alone. For alcohol made from molasses it is about 22 cents, and for that from potatoes about 21 cents. By the use of sawdust and other wood materials the cost of the raw materials can be reduced to 2 to 2.5 cents per gallon, the price depending upon the transportation and handling necessary. About ten years ago a method was devised by Dr. A. Classen for converting the cellulose of these waste materials partly into fermentable sugar by the action of sulphur dioxide and steam under pressure. While the process worked successfully on an experimental basis certain defects developed when it was used on a commercial basis which rendered it unprofitable.

This lack of success was due (*a*) to the fact that it required from four to six hours to digest one and a half to two tons of material; (*b*) to the formation of large amounts of sulphuric acid which caused the production of gums and caramel and made the extraction of the sugar a long and expensive process; and (*c*) to the delay and expense due to the injury of the lead lining of the converter. Since the use of this process

[1] R. F. Ruttan: J. Soc. Chem. Ind., **28**, 1290 (1909).

[2] W. P. Dreaper: *Ibid.*, **28**, 1297 (1909). A. Colin: Rev. Gén. Chimie, **12**, 40 (1909).

was abandoned engineers and chemists have been conducting experiments and have succeeded in overcoming the difficulties mentioned above, thus making the process thoroughly practical. By reducing the time of digestion to forty-five minutes they have reduced the amount of sulphuric acid and gums formed, and by lining the digester with fire-brick have increased the life of the apparatus. The digester now used is of steel with the fire-brick lining set in a cement of lead oxide and glycerol and measures 12 by 8 feet. The sulphur dioxide and steam are introduced through a perforated pipe which passes through the trunnions of the cylinder. After the digestion is complete the material is extracted and the solution is fermented and distilled, some malt being added to furnish food for the yeast. The alcohol obtained is clear, has no odor nor flavor of wood, contains no methyl alcohol nor fusel oil, but does contain slight traces of furfurol and aldehyde. Thus far no efforts have been made to reclaim the turpentine and acetic acid which are also extracted; but this problem will no doubt receive attention at the proper time. At present the residue left after the extraction is pressed into cakes, partly dried and used as fuel.

The author estimates that a plant with a capacity of 200 tons of sawdust per day can produce alcohol at a net cost of 10.8 cents per gallon, while the Alcohol Co. claim that they can produce it for 7 cents. Denatured alcohol costs the consumer 45 to 60 cents, while it should not cost him more than 20 to 25 cents.

It is generally assumed that the formation of sugars is due to the hydrolysis of the cellulose element of the wood. A number of chemists have pointed out that the average composition of wood, with the exception of several hard woods, is:

	Per cent.
Cellulose and oxycellulose material	65
Noncellulose material	35

In the production of alcohol by this method about 35 per cent. of the material, corresponding to the amount of noncellulose material present, is converted into sugar, while the residue of cellulose, amounting to 65 per cent. of the original material, does not yield sugar even when treated again in the same way, nor does a true fibrous cellulose (absorbent cotton) show any action when treated in a similar manner. It would therefore appear that, under the conditions of these

experiments, the true cellulose and the oxycellulose are not seriously altered chemically, while the lignone complex is capable of yielding sugar.

Should this prove to be the case, it might be possible to obtain alcohol from wood pulp and then use the residue (65 per cent. of the original) for the preparation of paper.

While the production of artificial silk has been suggested by several persons, the real birth of this industry was due to Count de Chardonnet, who, with the results described in a sealed document, deposited with the Academy of Sciences of Paris in 1884 and opened in 1887, as a basis, had so developed his method as to win a Grand Prix at the Paris Exposition of 1889. From that time the work has gone on steadily but slowly, as enormous difficulties had to be overcome before the industry could be placed on a paying basis. Many of the details of the methods are necessarily secret, as they could not be protected by patent.

One of the difficult problems, which has, however, been solved within the past year, was the recovery of the alcohol and ether from the wash liquors. As several liters of alcohol are used in the production of each kilogram of silk, the recovery of the solvents becomes a matter of the greatest importance.

Three methods for the preparation of artificial silk are in use at the present time on the large scale, *viz.*, the nitrocellulose, the cuprammonium and the viscose methods. In the first method, the nitrocellulose is dissolved in alcohol and ether; in the second the cellulose is dissolved in an ammoniacal copper solution; and, in the third, the mercerized cellulose is dissolved in carbon disulphide.

The viscous solution, after standing for some days (5 to 15), is filtered under pressure to remove the air and make a homogeneous mixture and is then squirted through tubes or holes, 0.05 to 0.2 mm. in diameter, under a pressure of 10 to 15 atmospheres. The material comes out in the form of threads which are at once passed through a liquid bath to wash the material and decompose the cellulose compound. The threads of cellulose produced by this decomposition are wound on spools or bobbins and dried. During the decomposition process the threads lose not only much of their strength and compactness, but also about 30 per cent. of their weight. Material made from these threads has many of the properties of natural silk. It has the peculiar rustle of silk and its brilliancy, but it is dyed with direct or cotton dyes. Some of

the threads of the artificial material are finer than those of the natural product and compare very favorably with the latter in strength; but most of the material used is of the coarser grades, being about twice the size of the natural silk thread. In the early days of the industry it seemed as if the threads would not find any use on account of their weakness, but this difficulty has been gradually overcome and the product has been constantly improved. This material has not displaced the natural silk but is sometimes mixed with it and is used for a large variety of articles, in many cases leading to the production of entirely new products. It has been used very extensively for making braid and for a heavy cloth, for the preparation of filaments for lamps, for dies, castings, etc. It has been in such demand that the output has been sold six months ahead. Some figures as to the growth and present condition of the industry will give an idea of its constantly increasing importance:

Year.	Amt. produced in kg.
1896	600,000
1906	1,700,000
1909	4,000,000

The production of the natural silk in 1909 has been estimated to be 20,000,000 kilograms, or only five times as much as that of the artificial product. J. ELLIOTT GILPIN.

REVIEWS.

THE FUNDAMENTAL PRINCIPLES OF CHEMISTRY. An Introduction to all Text-books of Chemistry. By WILHELM OSTWALD. Authorized translation by HARRY W. MORSE. New York, London, Bombay and Calcutta: Longmans, Green & Co. 1909. pp. 349.

The aim of the book is thus stated by Ostwald in his preface: "Two tasks are set for the workers in any science. One of these is to enrich the chosen field by the discovery of new facts and the statement of new experiences. The other task is no less important, but its value is perhaps not so evident at first glance. It is to arrange the facts already known in the best order and to bring out the relations between them as clearly as possible. Whenever progress in the first of these tasks has been rapid, the second becomes the more necessary, for it offers the only possible way of attaining mastery over the manifold separate experiences and of bringing the science as

a whole into a convenient and serviceable form. * * * The present book has for its object the presentation of the actual fundamental principles of the science of chemistry, their meaning and connection, as free as possible from irrelevant additions. * * * Questions concerning fundamental principles meet the teacher at every step, and the mental character of the developing chemist is frequently determined by the way in which they are answered. * * * The book should be a guide to the teacher. It may serve to show him how such generalizations are to be handled and how they can be woven into his daily instruction in elementary chemistry. Generalizations are the fundamental base of the chemical symphony; and the various separate facts may be varied according to need or desire. To make use of another simile—generalizations are the bony skeleton of the chemical body, and the teacher must always let the bones appear through the individual chemical facts if he wishes to make of his teaching a true work of art."

The book comprises eleven chapters. The first deals with Bodies, Substances and Properties; the second with the Three States; the third with Mixtures, Solutions and Pure Substances; the fourth with Change of State and Equilibrium; the fifth with Solutions; the sixth with Elements and Compounds; the seventh with the Law of Combining Weights; the eighth with Colligative Properties; the ninth with Reaction Velocity and Equilibrium; the tenth with Isomorphism; and the eleventh with the Ions.

This work, like every one that comes from the pen of this great man, is full of suggestion and it is to be hoped that it will be read by a large number of those for whom it was written.

The work of the translator is admirably done. H. C. J.

A TEXT-BOOK OF PHYSIOLOGICAL CHEMISTRY FOR MEDICAL STUDENTS. By JOHN H. LONG, M.S., Sc.D., Professor of Chemistry in Northwestern University Medical School, Chicago. Second edition, revised. With 42 illustrations. Philadelphia: P. Blakiston's Son & Co. 1909. pp. viii + 396. Price, $2.50.

The first part of this book deals with the various factors

concerned in digestion and metabolism, and the first four chapters are devoted to a consideration of the various nutritive substances, including the inorganic elements of water, air and salts. Another chapter is given up to a discussion of the carbohydrates and related bodies, and another to the fats and protein substances and their derivatives. In the next five chapters the author discusses the presence and action of ferments in the various organs and their relation to the different digestive processes.

The second part of the book deals with the various excretions of the body and gives different methods for their examination. Attention is called to the chemistry of the blood and various tissues, and the excretions of the various organs of the body, including all the more important end-products, are described at length. The author also devotes several chapters to the discussion of special topics, all of which are interestingly written. Perhaps the most interesting of these is the one which treats of the special properties of blood serum and its relation to immunity.

Although the author states in his preface that this book is intended to be a brief review of the important principles of physiological chemistry, in his endeavors to be brief he has not sacrificed any of the essential details necessary to a comprehensive understanding of the entire subject. The book is well written and not only appeals to the student of medicine but to all interested in physiological chemistry.

A MANUAL OF VOLUMETRIC ANALYSIS, Treating on the Subjects of Indicators, Test-papers, Alkalimetry, Including the Assay of Drugs by Titration, Acidimetry, Analysis by Oxidation and Reduction, Iodometry, Determinations by Precipitation, and by Color Comparison. By VIRGIL COBLENTZ, PH.D., PHARM.M., F.C.S., Professor of Chemistry in the New York College of Pharmacy. Second Edition, Revised, Completely Reconstructed and Enlarged, by ANTON VORISEK, PHAR.D., Professor of Analytical Chemistry in the College of Pharmacy, Columbia University. With 37 Illustrations. Philadelphia: P. Blakiston's Son & Co. 1909. pp. vii + 234. Price, $1.75.

This work now consists of a compact handbook primarily designed for the use of pharmacists. It comprises five chapters, the titles of which, as given, are "Introductory," "Determinations by Neutralization," "Determinations by Oxida-

tion and Reduction," "Determinations by Precipitation," and "Determinations by Comparison of Colors." An appendix contains atomic weight tables, and a list of elements and their most important compounds, with the molecular weights of the latter.

The procedures given are usually the better known and standard ones; the descriptions are concise but usually clear and reasonably adequate. Reactions are freely given, and calculations explained. The section on indicators is quite complete; that on ionic changes in solution is hardly adequate as a treatment of that subject. As a handy volume of sufficient scope to serve as a guide in the more frequently occurring lines of analysis, this work deserves the attention of pharmacists, for whom, as already stated, it is primarily written.

H. P. TALBOT.

RECHERCHES SUR LA PRÉPARATION ÉLECTROLYTIQUE DES COMPOSÉS DU PLOMB. Par CARL DUVIVIER, Ingénieur. Malines: L. et A. Godenne. 1909. pp. 19.

The electrolytic preparation of insoluble compounds from soluble anodes has so far been industrially successful only with lead. The pamphlet under notice deals with the research carried on by the author in the preparation of lead paints by the electrolytic solution of pure lead and its precipitation as basic carbonate, chromate, monoxide, sesquioxide and peroxide. While the preparation of white lead is carried on industrially according to the process of Luckow, the manufacture of other lead compounds by the aid of electrolysis of lead has so far been a commercial failure. The author reviews the white-lead processes of Hoosick, Luckow and Brown, which he has also tested, and then gives the detail of his own work, which is shown to have furnished good results.

H. O. HOFFMAN.

DIE ELECTROCHEMISCHEN VERFAHREN DER CHEMISCHEN GROSS-INDUSTRIE. Ihre Prinzipien und ihre Ausführung. Von DR. JEAN BILLITER, Privatdozent an der Universität Wien. I Band. Electrometallurgie wässriger Lösungen. Mit 117 Figuren und vielen Tabellen im Text. Halle a. S.: Druck und Verlag von Wilhelm Knapp. 1909. pp. vii + 284. Price, M. 12.

The present volume, dealing with the electrometallurgy

of aqueous solutions, is the first of a proposed series of four which is to cover the whole field of industrial electrochemistry; the three remaining volumes are to be entitled: Electrolysis of Aqueous Solutions with Insoluble Anodes; Electrolysis of Fused Salts; and Electric Furnaces. The aim of these publications is not only to describe the present state of the different electrochemical industries, but to discuss the processes critically according to principles of modern electrochemistry.

The volume under consideration treats of the metals copper, silver, gold, lead, zinc, tin (detinning tinplate), nickel, bismuth, cadmium, quicksilver, and the preparation of metallic compounds. It begins with a review of the electrolytic laws, which are sketched briefly and put in such a way as to be readily understood by the reader not fully at home in the ionic theory. The method chosen for presenting the electrometallurgy of the several metals is to take up first principles and then practice. Thus, in the electrolytic refining of metallic copper, the general principles are discussed under the heading of electrolysis of pure anodes; the behavior of impurities is then treated under impure anodes; a critical review of the matter in the two preceding sections furnishes the occasion for giving general rules that ought to govern practice; and lastly comes the consideration of efficiency. For the review of actual work, some leading examples of the multiple- and series-systems are given and a comparison of the two is made; then follows the working-up of fouled solutions and of anode-mud, and lastly comes a brief description of the necessary analytical determinations. The general plan of treatment is excellent and the same is true of the discussion of principles. The presentation of the practice cannot be praised so unreservedly. While many details of different plants are recorded in a systematic manner, others of importance are missing; of the 117 illustrations given in the text, in only one set (Figs. 103–106) are dimensions given; the photographic reproductions of parts of plants are so inferior as to have next to no value even as pictures.

In the second main division of copper, the electrolytic treatment of copper compounds, the processes of Marchesi, Hoepfner and Siemens are treated briefly, and with reason, as they have been failures; but there is no mention of the successful electrolysis of pure copper matte with the recovery of sulphur as carried out in the Mansfeld district. Of the electrolytic production of articles of commerce (tubes, etc.), probably too little is known at large to make the third and last division comprehensive.

In the parting of doré silver, also, many important details, descriptive as well as constructive, which are available through the technical literature deserve to be mentioned. In the recovery of gold from cyanide solutions the practice of Siemens and Halske, as described in the book of von Uslar in 1903, and reproduced here, has been considerably modified and supplemented. Similar remarks might be made regarding some of the remaining metals.

Taking the book as a whole, there is presented a volume which is excellent in arrangement, in presentation of principles, and in discussion of processes from the point of view of modern electrochemistry; the treatment of actual practice requires some revision to bring it to the standard of that of principles. The electrochemist makes himself felt everywhere in the book, the engineer is less evident. The metallurgist will find the volume the best guide that has been presented so far for the study of principles of the various electrolytic processes he may have to deal with; the electrochemist will obtain a better introduction into actual practice than is usually furnished in books dealing with the subject.

H. O. Hofman.